

S
549.7
M43i



PLEASE RETURN

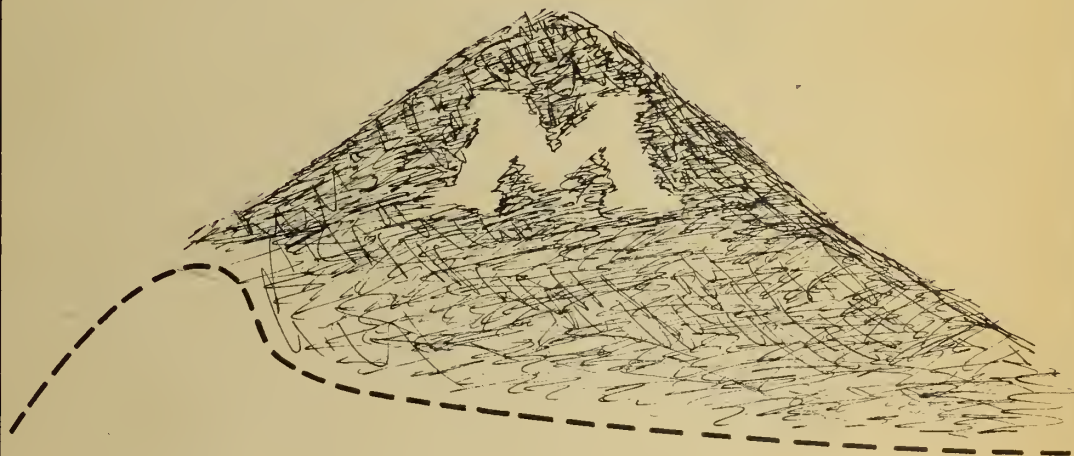
STATE DOCUMENTS COLLECTION

MAY 24 1978

MONTANA STATE LIBRARY
930 E Lyndale Ave.
Helena, Montana 59601

AN INVESTIGATION OF
ASPHALT-AGGREGATE ADHESION
BY MEASUREMENTS OF HEATS
OF IMMERSION

by
E. KEITH ENSLEY
and
HENRY A. SCHOLZ



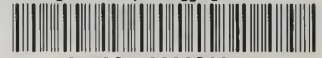
MONTANA COLLEGE OF MINERAL
SCIENCE AND TECHNOLOGY
BUTTE, MONTANA

Research Project
Item 20, HPR-1(6)

MONTANA STATE LIBRARY

S 549.7 M43i c.1 Ensley

An investigation of asphalt-aggregate ad



3 0864 00008631 7

MONTANA COLLEGE OF MINERAL SCIENCE AND TECHNOLOGY

Butte, Montana

Final Report

Research Project: Item 20, HPR-1(6)

AN INVESTIGATION OF ASPHALT-AGGREGATE ADHESION
BY MEASUREMENTS OF HEATS OF IMMERSION

By

E. Keith Ensley

and

Henry A. Scholz

Prepared for

Montana State Highway Commission
Planning Survey Section

In cooperation with

U.S. DEPARTMENT OF TRANSPORTATION
Federal Highway Administration
Bureau of Public Roads



Digitized by the Internet Archive
in 2013

<http://archive.org/details/investigationofa00ensl>

ACKNOWLEDGMENTS

The authors are indebted to Mr. Donald McGlashan, Head of the Department of Mineral Dressing at Montana College of Mineral Science and Technology and Mr. Stephen Weber, Senior Assistant Materials Engineer with the Montana Highway Commission, for their valuable discussions. We also wish to thank Mr. John Cavanaugh for his assistance in data acquisition and calculations. Mrs. Helen McLaughlin is due recognition for her typing of this report and other reports required through the course of the project.

The opinions, findings and conclusions expressed in this publication are those of the authors and not necessarily those of the Bureau of Public Roads.

PREFACE

This is a final report on two years of investigation on the project "An Investigation of Asphalt-Aggregate Adhesion by Measurements of Heats of Immersion" conducted by the Department of Chemistry, Montana College of Mineral Science and Technology sponsored by the Montana State Highway Commission in cooperation with the U. S. Bureau of Public Roads.

The research was under the supervision of Dr. K. Ensley, Associate Professor of Chemistry. Construction of the microcalorimeter by H. Scholz, graduate student in Mineral-Dressing Engineering and Ensley was completed in the first phase, June 1966-June 1967, and a few preliminary tests were begun. The project was renewed in June 1967 for one year. Reduction to routine testing was accomplished in the fall of 1967 and since that time meaningful data has been collected. John Cavanaugh joined the project in September 1967.

TABLE OF CONTENTS

| | Page |
|--|------|
| ACKNOWLEDGMENTS - - - - - | ii |
| PREFACE - - - - - | iii |
| TABLE OF CONTENTS - - - - - | iv |
| LIST OF FIGURES - - - - - | vi |
| INTRODUCTION - - - - - | 1 |
| A Brief Review of Asphalt - - - - - | 1 |
| Adhesion - - - - - | 4 |
| Adhesion and Cohesion in Contact Angle Studies - - - - - | 8 |
| Microcalorimeters and Heats of Immersion - - - - - | 11 |
| CONSTRUCTION OF THE MICROCALORIMETER - - - - - | 15 |
| General Description of the Assembly - - - - - | 15 |
| Oven - - - - - | 15 |
| Heat Sink - - - - - | 17 |
| Copper-Constantan Thermopile Assembly - - - - - | 20 |
| Reaction Cell and Holder - - - - - | 20 |
| Radiation Can and Shield - - - - - | 22 |
| Calibration Cell - - - - - | 22 |
| Teflon Sample Holder - - - - - | 24 |
| Electroplating - - - - - | 24 |
| Anodization - - - - - | 25 |
| PROCEDURE AND RESULTS - - - - - | 26 |
| Experimental Procedure - - - - - | 26 |
| Discussion of Results - - - - - | 27 |

| | page |
|---|------|
| GENERAL CONCLUSIONS - - - - - | 43 |
| SPECIFIC CONCLUSIONS - - - - - | 43 |
| RECOMMENDATIONS - - - - - | 44 |
| RECOMMENDATIONS FOR FUTURE HEATS OF IMMERSION STUDIES - - - - - | 44 |
| LIST OF REFERENCES - - - - - | 45 |

LIST OF FIGURES

| Figure | | Page |
|--------|---|------|
| 1 | A vector representation of contact angles - - - - - | 8 |
| 2 | Hydration of tricalcium silicate - - - - - | 13 |
| 3 | Immersion of sodium aluminate in water - - - - - | 14 |
| 4 | Top view of microcalorimeter - - - - - | 16 |
| 5 | Cross section of heat sink - - - - - | 18 |
| 6 | Cross section of thermopile - - - - - | 19 |
| 7 | Various microcalorimeter components - - - - - | 21 |
| 8 | Calibration coil - - - - - | 23 |
| 9 | Calorimeter response and calibration - - - - - | 28 |
| 10 | Calibration curve - - - - - | 29 |
| 11 | Immersion of pure quartz in untreated asphalt - - - - - | 32 |
| 12 | Immersion of pure quartz into asphalt treated with metal- amine - - - - - | 33 |
| 13 | Immersion of pure quartz into asphalt treated with metal- amine - - - - - | 34 |
| 14 | Immersion of a slag in asphalt - - - - - | 35 |
| 15 | Immersion of slag in metal-amine treated asphalt - - - - - | 36 |
| 16 | Immersion of Glacier County No. 1 aggregate in asphalt - - - | 37 |
| 17 | Immersion of Lewis and Clark County aggregate in asphalt - - | 38 |
| 18 | Immersion of Lewis and Clark County aggregate in metal-amine treated asphalt - - - - - | 39 |
| 19 | Immersion of Glacier County No. 3 aggregate in asphalt - - - | 40 |
| 20 | Immersion of Teton County aggregate in asphalt - - - - - | 41 |
| 21 | Immersion of pure calcite in asphalt - - - - - | 42 |

INTRODUCTION

A BRIEF REVIEW OF ASPHALT

Asphalt is one of man's oldest building materials. It may have been first used, not for construction, but by our ancestors to trap game in the tar pits. The early shipbuilders used it for calking, bricklayers used it for mortar. It was also used by our ancestors for decoration of buildings, swimming pools, mummification, fuel, painting and even building roads (1,2,3).

Because of its complex nature it will continue to offer challenges to many facets of science. Its chemical building blocks have been difficult to separate and identify. Perhaps more success has been in physical testing rather than in chemical identification.

To complex the picture further, its chemical and physical characteristics are functions of the geographical location of the asphalt. The ratio of the principal constituents carbon, hydrogen, nitrogen, sulfur and oxygen vary several per cent throughout the world or even within the same regions. Also the per cent of aromatics, napthenes and paraffins differ with each deposit.

Metals such as vanadium, iron, and magnesium have been observed in many asphalts. These elements are probably bonded in porphyrine rings as metal chelates.

Such a variety of constituents gives rise to the possibility of many types of bonding both in adhesion and cohesion in asphalt systems.

Numerous methods have been applied to understanding, modifying and characterizing asphalts. The following list includes many of the various tools or methods used in asphalt studies (4).

1. Penetration tests
2. Strip tests
3. Shear rate
4. Compression tests
5. Chemical analysis
6. Viscosity measurements
7. Surface tension measurements
8. Ductility tests
9. Contact angle measurements
10. Solubility studies
11. Nuclear magnetic resonance
12. Neutron activation analysis
13. Infrared spectroscopy
14. Electron spin resonance
15. Dielectric studies
16. Electron microscopy
17. X-ray spectroscopy
18. Mass spectroscopy
19. Streaming potentials
20. Inverse chromatography
21. Road survival time

Even with such a diversified attack on the problems of asphalts and their adhesion to aggregates, more fundamental research is required.

For example, the strip test method used in testing the asphalt-aggregate bond relies upon human judgement with a considerable amount of approximating required. Contact angle measurements, which will be discussed in detail later, often aid in adhesion studies, but have born little fruit in asphalt-aggregate systems.

Thermodynamics has found little application in asphalt technology. Although it is one of the older areas in science, it continues to offer a penetrating and refreshing view into chemical and physical changes. The instrumentation required to measure the energy released in chemical changes, although it may be quite elaborate, usually does

not have to be as sensitive as those required to detect the small amount of energy released in physical changes. Adhesion, without chemisorption, is classed as a physical change.

Because this report is concerned with adhesion and the energy released during the adhesion process a brief review on the theory of adhesion as applied to asphalt-aggregate systems will be discussed and followed by the instrumentation required to detect the energy of adhesion.

ADHESION

Man has also observed the phenomena of adhesion for centuries but only recently has he begun to measure their magnitude and propose theories to unify his observations in mathematical form (5,8,9,10,11,12,13,14,18,24,26).

Cohesion occurs within a phase and pertains to the force between molecules within that phase. Adhesion occurs at phase boundaries and is concerned with the force between the particles at the boundaries. The understanding of both phenomena should aid in the elucidation of the mechanism in the bonding present in asphalt-aggregate mixtures.

Several types of forces are probably involved in adhesion and cohesion in asphalt-aggregate mixtures.

- (1) Coulombic forces
- (2) Permanent dipole interactions
- (3) Induced dipole interaction
- (4) London dispersion forces

Resolving the mysteries of adhesion at the asphalt-aggregate interface is complexed by the many polar and non-polar compounds in asphalt as well as the variance in the aggregate surfaces.

It is best to avoid complexing the picture more than necessary and to discuss only the quartz surface and a few functional groups observed in asphalts.

The surface of silica under atmospheric conditions has been discussed by several authors. Snyder and Ward (17) point out that "the surface of a hydrated silica is covered with hydroxyl groups which are attached to silicon atoms and that these surface hydroxyls may be classified into two distinct types: free hydroxyls....and hydrogen

bonded (bound) hydroxy groups....infrared absorption studies suggest that the selective adsorption of polar molecules and aromatic hydrocarbons occurs primarily upon free hydroxyls."

Shulman (19) discusses the bonding between silica surfaces and functional groups as applied to flotation. He assumes a negative surface which has well been established by zeta and streaming potential measurements.

Ionic or dipole bonds between the asphalt and silica probably give rise to only part of the forces that exist. London (9) proposed that synchronization of electron densities could explain attractions between non-polarized particles. His theory on the dispersion forces has been extended into many areas of science from the original explanation of liquifaction of inert gases to the sticking of Scotch tape.

London postulated that electrons surrounding the atoms could set up harmonic oscillations in neighboring atoms which gives rise to interactions between instantaneous dipoles. Debye (26) has discussed the application of London's theory to adhesion and cohesion.

Such forces are probably present between asphalt and silica. In fact, since asphalt consists of so many species of molecules and atoms, probably most forces which have been postulated between solids and liquids are present in asphalt-aggregate bonds.

It is only natural to believe that the viscous properties and sticking characteristics of asphalt are due to macromolecules. Rowland (27) et. al. stated "that all adhesives are macromolecular in character." Molecular weights of various fractions in asphalts have

been found to range between 200 and 7000 or higher. Barth states that "micellar size" is more appropriate since molecular weight pertains only to pure substances.

As mentioned previously, asphalt contains a wide variety of elements. With the presence of elements with markedly different electronegativities one might speculate that functional groups with dipolar characteristics are responsible in part for adhesion and cohesion properties. The polar surface of quartz or quartz-like materials would aid in adsorption of polar molecules. For example, an amine polymer would probably attach itself to silica through $\text{NH}_2\text{-SiO}$ linkages. (See Ref. 27 for pictorial representations of macromolecular adsorption).

As molecules find an adsorption site they perhaps lose most of their translational energy although movement at the end of long molecules would persist. Once the sites have been occupied there is a possibility that polar sites along the molecules could aid in alignment of other molecules and probably several layers could build up at ordinary pressures in asphalt systems. London forces could also assist in multilayer build-up for molecules without polar groups.

If the reaction between an asphalt and an aggregate were followed by a calorimeter it would "see" the energy released in the adsorption process from (a) a loss in translational motion of molecules, (b) formation of bonds between asphalt and aggregates, (c) formation of bonds between aligned asphalt molecules, and (d) a decrease in entropy as observed in magnetic cooling.

The total energy for the above processes is termed heat of immersion. Harkins (5) defines the heat of immersion as equal to

the sum of three terms - heat of vaporization, heat of emersion, and heat of adsorption. The four sources above simply attempt to microscopically define the source of the energy while this latter macroscopic definition applies Hess's law to define immersion thermodynamically.

No attempt has been made in our investigation to determine independently any of the individual sources of energies, either microscopically or macroscopically; therefore, only the heat of immersion will be discussed.

Many of the expressions encountered in adhesion and cohesion can be clarified in a brief discussion of contact angles. Therefore, before pursuing immersion further, a discussion of the theory of contact angles is appropriate.

ADHESION AND COHESION IN CONTACT ANGLE STUDIES

Adhesion between a liquid and a solid can be investigated by one of several methods (7,8,10,12):

- a. Contact Angles
- b. Heats of Immersion
- c. Peel Tests
- d. Shear Impact Tests

The application of contact angles has been employed to asphalt-aggregate systems by several investigators (2:650).

The basic formula which relates the contact angle, θ , to surface tension, γ is given by equation 1.

$$\gamma_{s/v} = \cos \theta \gamma_{l/v} + \gamma_{s/l} \quad 1.$$

It is vectorally derived from the following diagram.

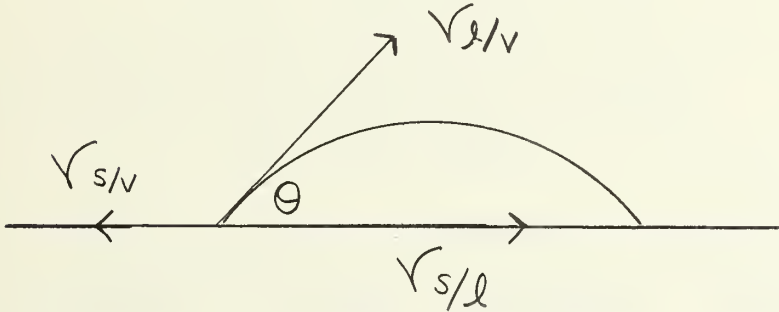


Fig. 1. A vector representation of surface tension between a wetting agent and the material being wetted.

The three phases vapor, liquid, and solid are represented by v, l and s. The terms $\gamma_{s/v}$, $\gamma_{s/l}$ and $\gamma_{l/v}$ are respectively interfacial tensions between solid and vapor, solid and liquid and liquid and vapor.

Another useful equation which defines the work of adhesion, $W_{s/l}$ is:

$$W_{s/l} = \gamma_{l/v} + \gamma_{s/v} - \gamma_{s/l} \quad 2.$$

Formula 1 implies surface tension as force per unit length and formula 2 implies surface tension as a measure of free energy per unit area, two equivalent units for γ .

The equation for work of adhesion can be transformed to work of cohesion by letting $\gamma_{l/v} = \gamma_{s/v}$ and $\gamma_{s/l} = 0$, for homogenous system. Or,

$$W_{l/v} = 2 \gamma_{l/v} \quad 3.$$

is the energy required to break a 1 cm^2 column of liquid and form two new surfaces in equilibrium with the vapor.

Attention can be focused upon both adhesion and cohesion through the spreading coefficient, $S_{s/l}$, demonstrated by Harkins (15).

$$S_{s/l} = \gamma_{s/v} - \gamma_{l/v} - \gamma_{s/l} \quad 4.$$

Or in terms of work of adhesion and cohesion,

$$S_{s/l} = W_{s/l} - W_{l/v}. \quad 5.$$

When $S_{l/s}$ is positive, spreading is accompanied by a decrease in free energy, or the process is spontaneous. Spreading is accompanied by a creation of a greater liquid surface and a decrease in the exposed solid surface as applied to the derivation of equation 4. Because of the low surface energies of most organic liquids we can expect them to spread freely on solids of high surface energy.

The spreading coefficient can be expressed in terms of measurable quantities by substitution of $\gamma_{s/v}$ in equation 1 into equation 4.

$$S_{s/l} = \gamma_{l/v} (\cos \theta - 1) \quad 6.$$

Or in terms of work of adhesion

$$W_{s/l} = \gamma_{l/v} (\cos \theta + 1) \quad 7.$$

It is therefore necessary to determine both the surface tension of the liquid and the contact angle between the solid and the liquid to calculate $S_{s/l}$ or $W_{s/l}$. But the contact angle is all that is required to measure, in a qualitative way, the attraction between the solid and the liquid.

According to the literature, not a great deal of work has been done using contact angles to measure asphalt-aggregate adhesion (2,4,20). Brown and Welby state "contact angle measurements (in asphalt systems) are fraught with difficulties". They discuss these in detail.

Heat of Immersion

What other possibilities are there? For many years bonding has also been approached through immersion studies. It is well known that energy is released when a solid is immersed into a liquid. Zettlemoyer (15) states "determinations of the average polarity of solid surfaces, site energy distribution or heterogeneity of solid surfaces, and heat of formation of double layers" are parameters in heat of immersion observations. It has also been observed that immersion energy is very sensitive to foreign material on the surface even in small quantities as well as sensitive to small amounts of additives to the adsorbate (material being adsorbed). Wade and Hackerman (21) showed that immersion data depends upon particle size also. Larger particles gave higher values for heats of immersion when expressed in units of ergs per square meter. They investigated

both polar and nonpolar absorbates and explain the anomalies through ion-dipole interactions.

The strength in using heat of immersion as a measure of bonding lies in its sensitivity to so many parameters. In this is also a weakness that in order to obtain reproducibility the investigator must use extreme caution with regard to purity and treatment of the absorbent and absorbate.

Surface chemists have assumed for many years the stronger the interaction between the solid and the liquid the greater will be the energy released upon immersion. This statement is the basis for our investigation between asphalt and aggregate. We extend the postulation to state that the greater the heat of immersion of the aggregate in the asphalt, the stronger the bond; therefore, the more durable the highway constructed from the respective mixture.

Microcalorimeters and Heats of Immersion

Most of the investigations in heats of immersion have applied the technique of microcalorimetry (6,7,8). Except for chemisorption the energy released in sorption processes is usually quite small and requires very sensitive detection instruments.

Typical detectors employed are thermistors and thermocouples. Tian introduced the microcalorimeter using a single thermopile (an assembly of thermocouples). Later Calvet introduced differential microcalorimetry by connecting two thermopiles in opposition and increased the stability (6).

To increase the sensitivity further Benzinger applied the electroplating principle (22,23) to form several thousand thermocouples (The Benzinger Calorimeter is now produced by Beckman Instruments).

The later calorimeter can be used in an environment up to 70°C only. For asphalt work it is necessary to work well above this range and therefore, it was necessary to construct a higher temperature calorimeter to study asphalt-aggregate adhesion. The details of the construction appear in a following section.

A discussion of a few heats of immersion curves obtained from microcalorimeter studies will illustrate their value in various fields and show how certain observations may be of value in asphalt-aggregate adhesion research.

In Fig. 2 is seen the curve produced when sodium aluminate is immersed into water (6). The initial peak is attributed to the characteristic adsorption process. The second rise, it was postulated, was due to the formation of the trihydrate of alumina.

The curve seen in Fig. 3 was produced by the immersion of tricalcium silicate into water in cement investigations. It was noted that the first peak was proportional to the quantity of lime present in the final solution and the second peak to the quantity of anhydrous product used.

We observe that immersion studies give rate of reactions as well as the energy released for any given time. The shape of the curve was also sensitive to additives and temperature. Calvet states "applications of the microcalorimeter in experimental science are almost numberless". Perhaps it will find a place in highway construction.

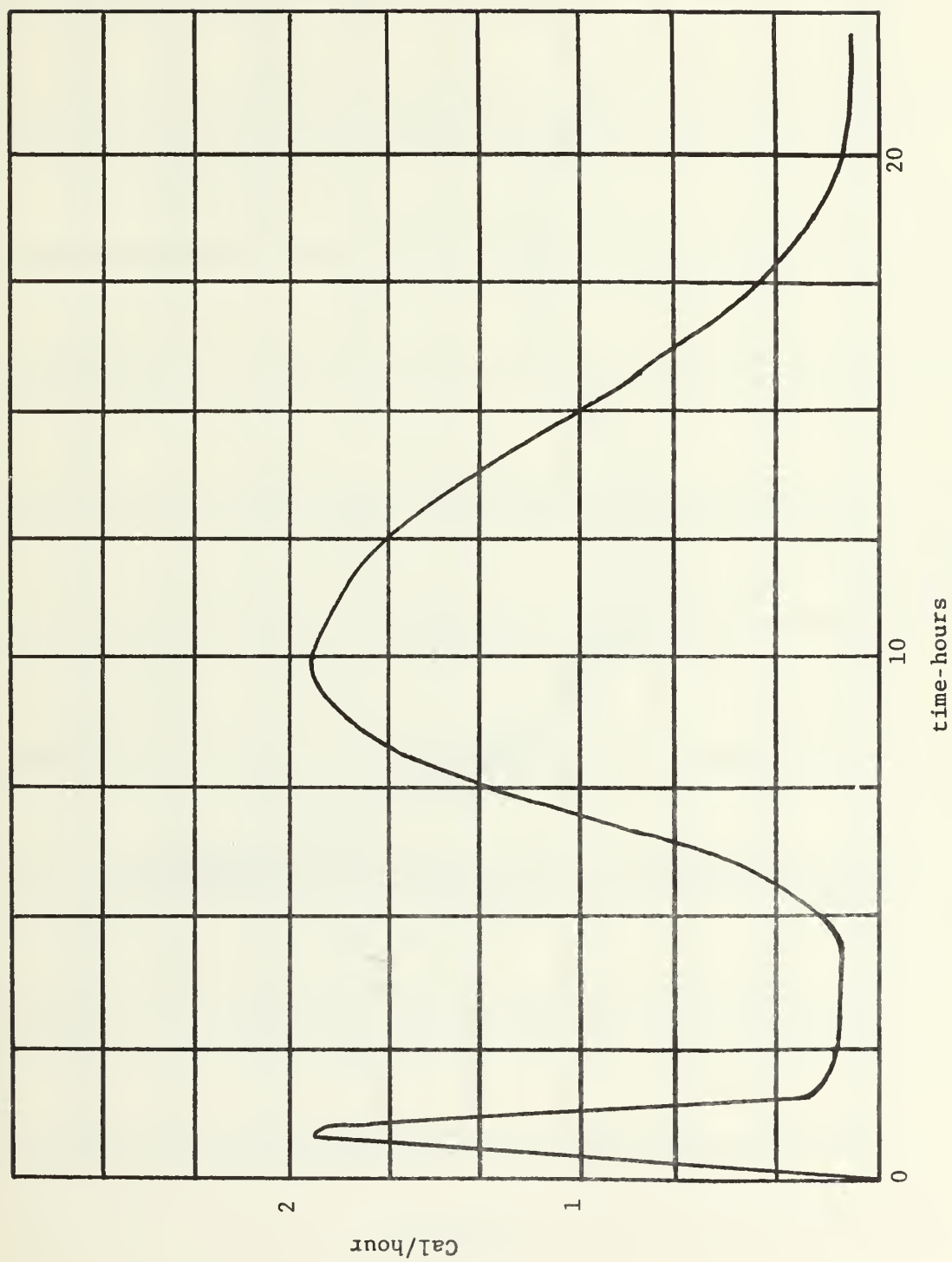


Fig. 3. Hydration of Tricalcium Silicate.

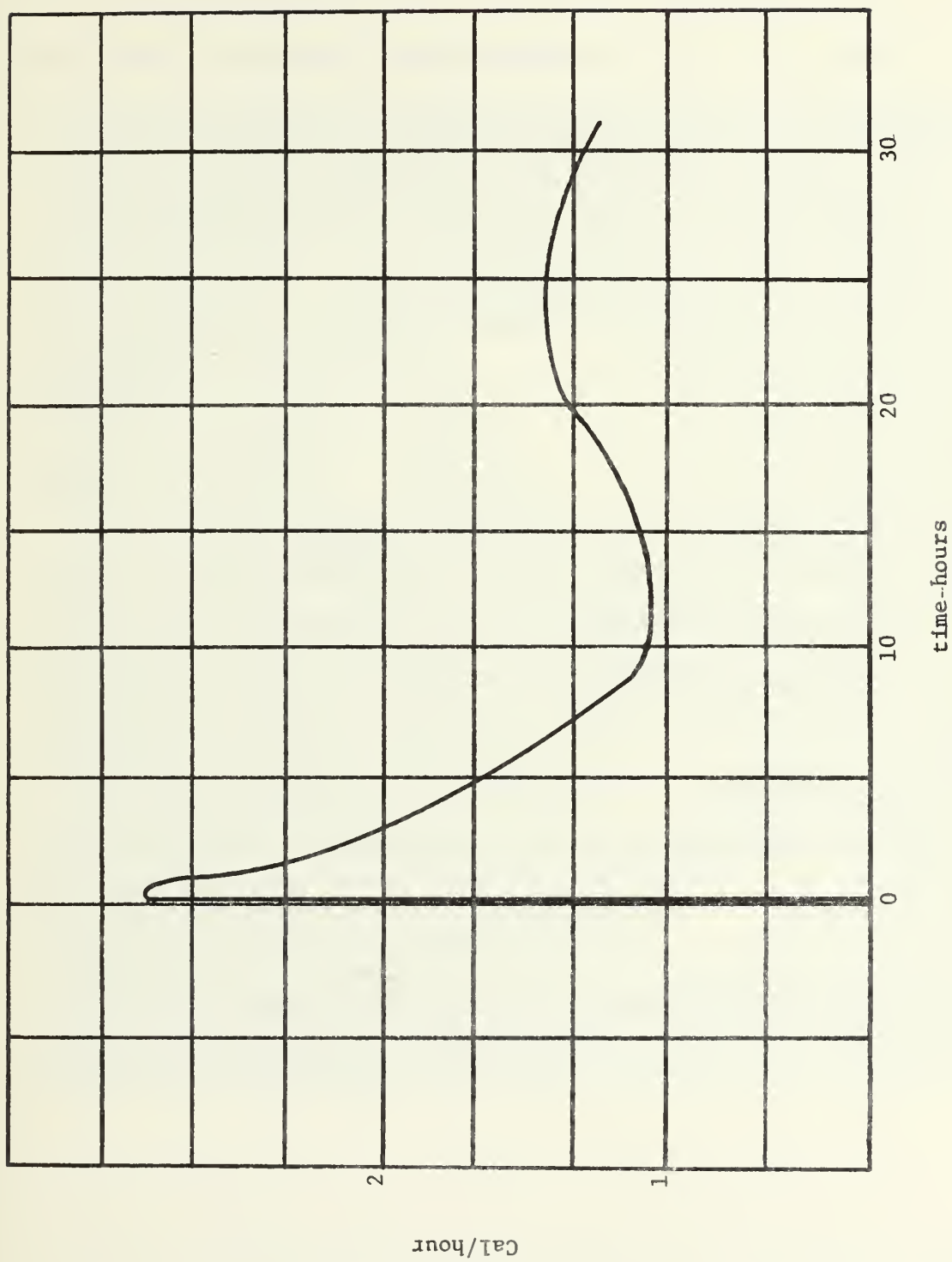


Fig. 2. Immersion of Sodium Aluminate in Water.

CONSTRUCTION OF THE MICROCALORIMETER

General Description of the Assembly

The microcalorimeter being used for our investigation is a differential Tian-Calvet type calorimeter. (Fig. 4) It consists of two cells surrounded by thermopiles which are connected in opposition; one cell serves as a reaction cell and the other as a blank. The energy released during the reaction is detected by the thermopile, which feeds a signal into a milli-microvoltmeter and onto a recorder. The rate and amount of energy released are determined from the curves produced.

Oven

The constant temperature oven, constructed from 1/8 inch steel, has the following dimensions: 32" x 32" x 32". It is insulated with 2 3/4 inches of vermiculite held in place by 1/2 inch Marinite paneling. The oven lid has a removable section which facilitates the accessibility of the microcalorimeter contained inside.

The oven is heated by four heating coils, of which three remain on continuously. The temperature is regulated by a thermistor which, controlled by a relay system, activates the fourth coil to keep the temperature constant within $\pm 0.05^{\circ} \text{C}$.

The air in the oven is circulated around the microcalorimeter by two fans, one on each side of the oven.

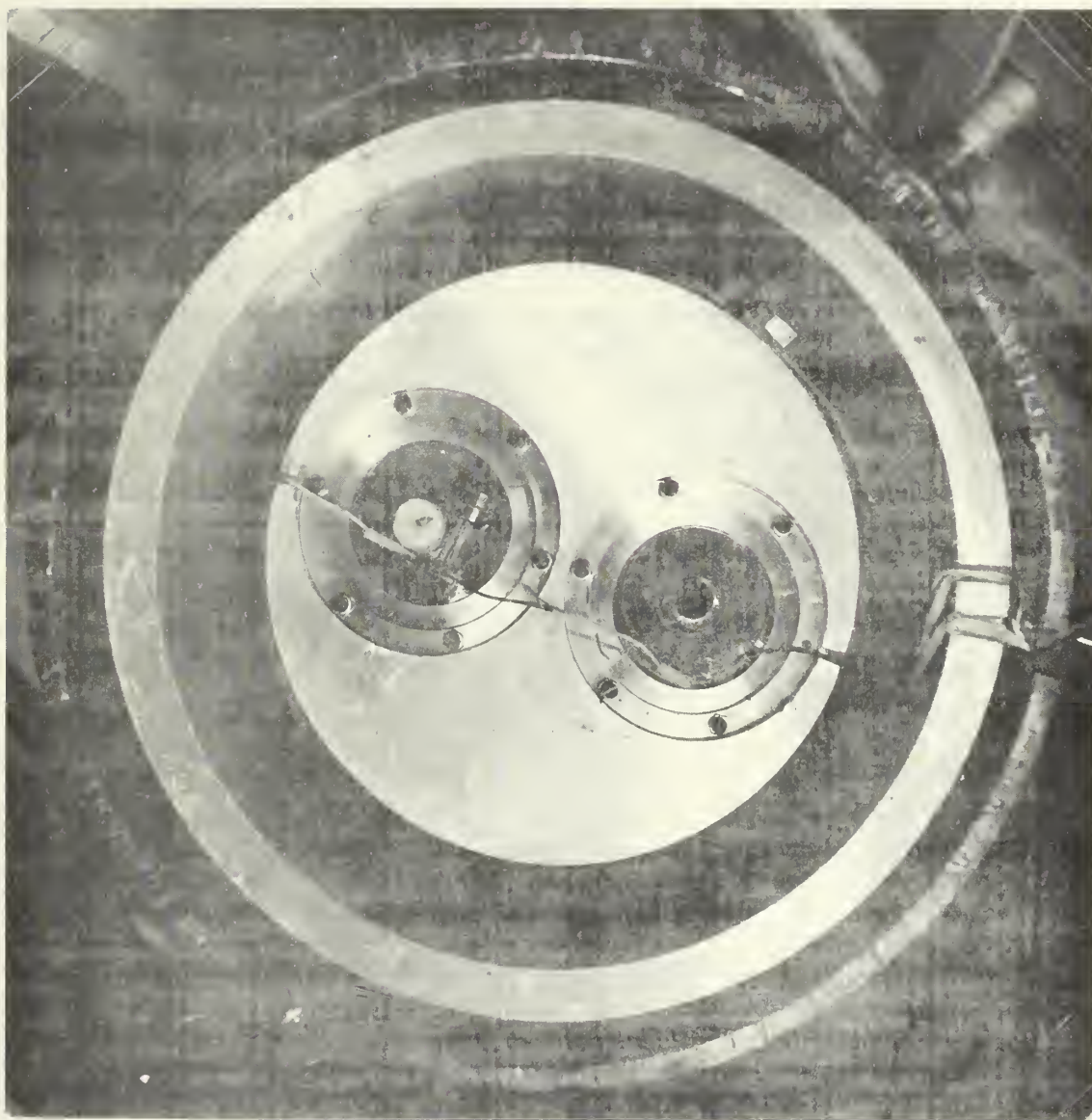


Fig. 4. A top view of the microcalorimeter with the reaction cell removed but the blank cell remaining. Lids are also absent.

Heat Sink

The aluminum heat sink (Fig. 5) is of the general Tian-Calvet type, which has been altered to our specifications. The sides of the two wells in the heat sink were constructed with a slight slope (1:8) to accomodate two hollow sleeves with a slope corresponding to their outer walls. The inner walls of the sleeves are cylindrical to fit around the thermopile (Fig. 6).

The oppositely connected cells of the microcalorimeter are similarly constructed, as in Differential Thermal Analysis, and the signal recorded by the instruments is the difference produced by the two cells.

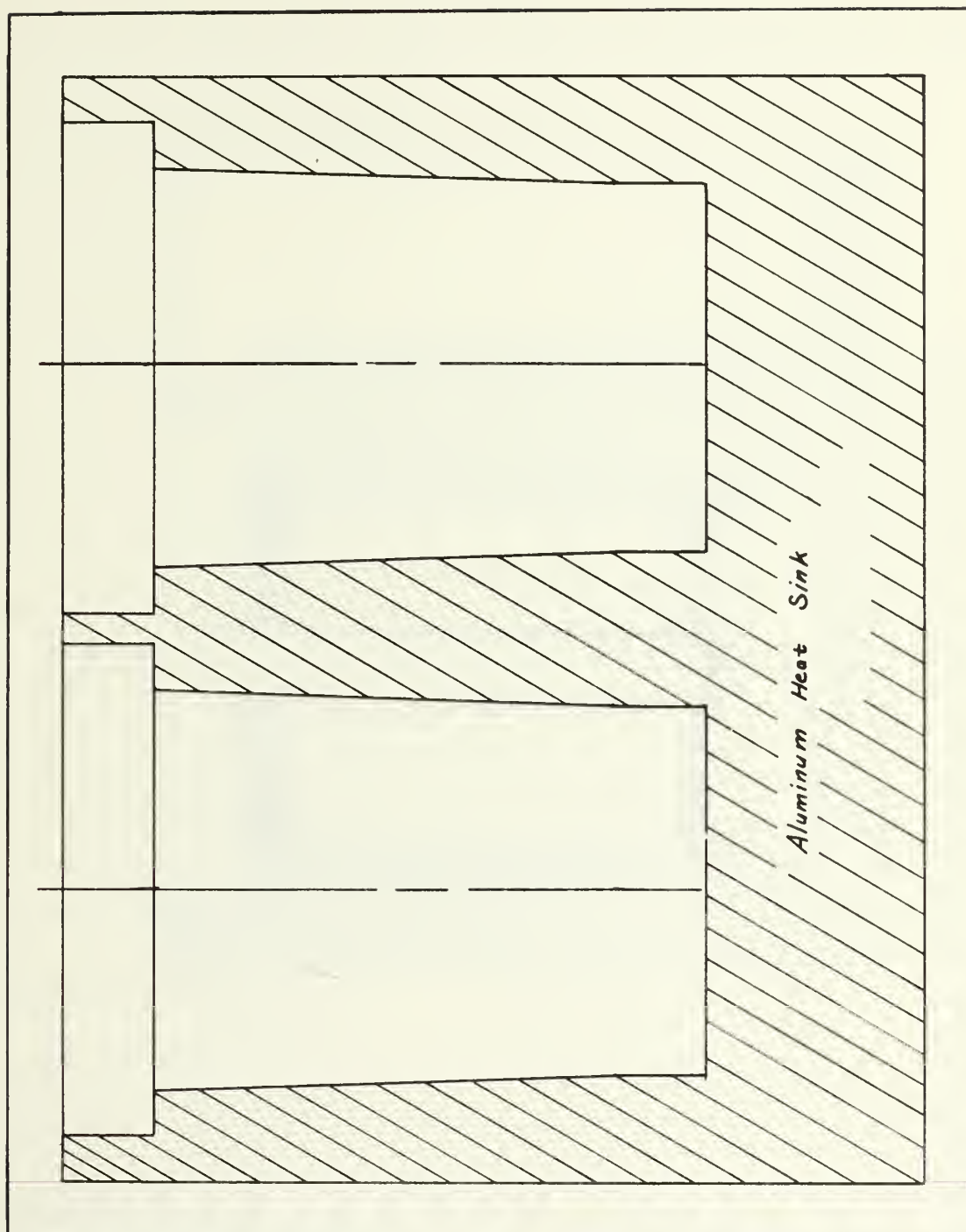


Fig. 5

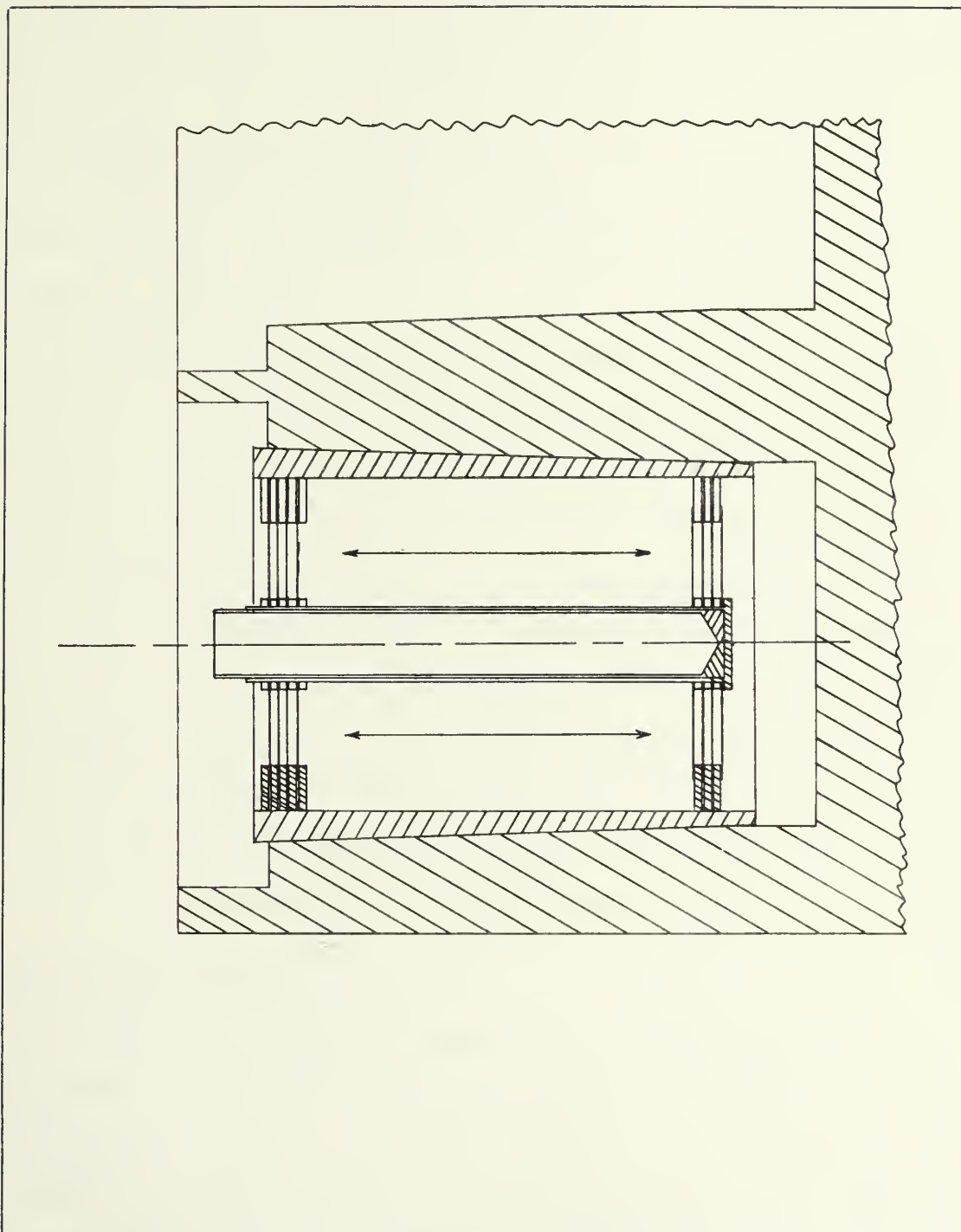


Fig. 6. Cross-section of the reaction cell and thermopile assembly. The ring holding the assembly in place and seen in the photograph is not shown.

Copper-Constantan Thermopile Assembly

The heart of the instrument is the two copper-constantan thermopiles. They were constructed by wrapping a continuous 30 gauge constantan wire around a mica wafer 25 to 35 times. One side of the disk was then coated with fingernail polish and glue, and copper was electroplated on the bare constantan wire in a copper cyanide bath. The protective coating was removed, leaving a series of copper-constantan thermocouples which are 40% efficient as a welded copper-constantan thermocouple.

Each thermopile is composed of approximately 1,120 thermocouples (450 effective) contained on approximately 40 mica wafers. The inner junctions serve as the hot junctions and the outer serve as the cold junctions. The hot junctions surround, and are in direct contact with, the anodized cell holder (Fig. 7e) in which the reaction cell is placed (Fig. 7d). Each mica disk is held in place by small anodized aluminum rings (Fig. 7c) and insulated from other disks by a mica washer. The cold junctions are held in place by large anodized aluminum rings (Fig. 7b) around which is compressed one of the tri-sectional hollow sleeves which has been anodized on the inside wall. One of the assembled cell compartments can be seen in Figure 6.

Reaction Cell and Holder

In order that the reaction vessel could be cleaned after each experiment, a system had to be developed which would facilitate the removal of the reaction vessel without thermally upsetting the system. A thin-walled aluminum reaction cell (Fig. 7d) was fabricated to fit tightly inside an equally thin-walled cell holder (Fig. 7e).

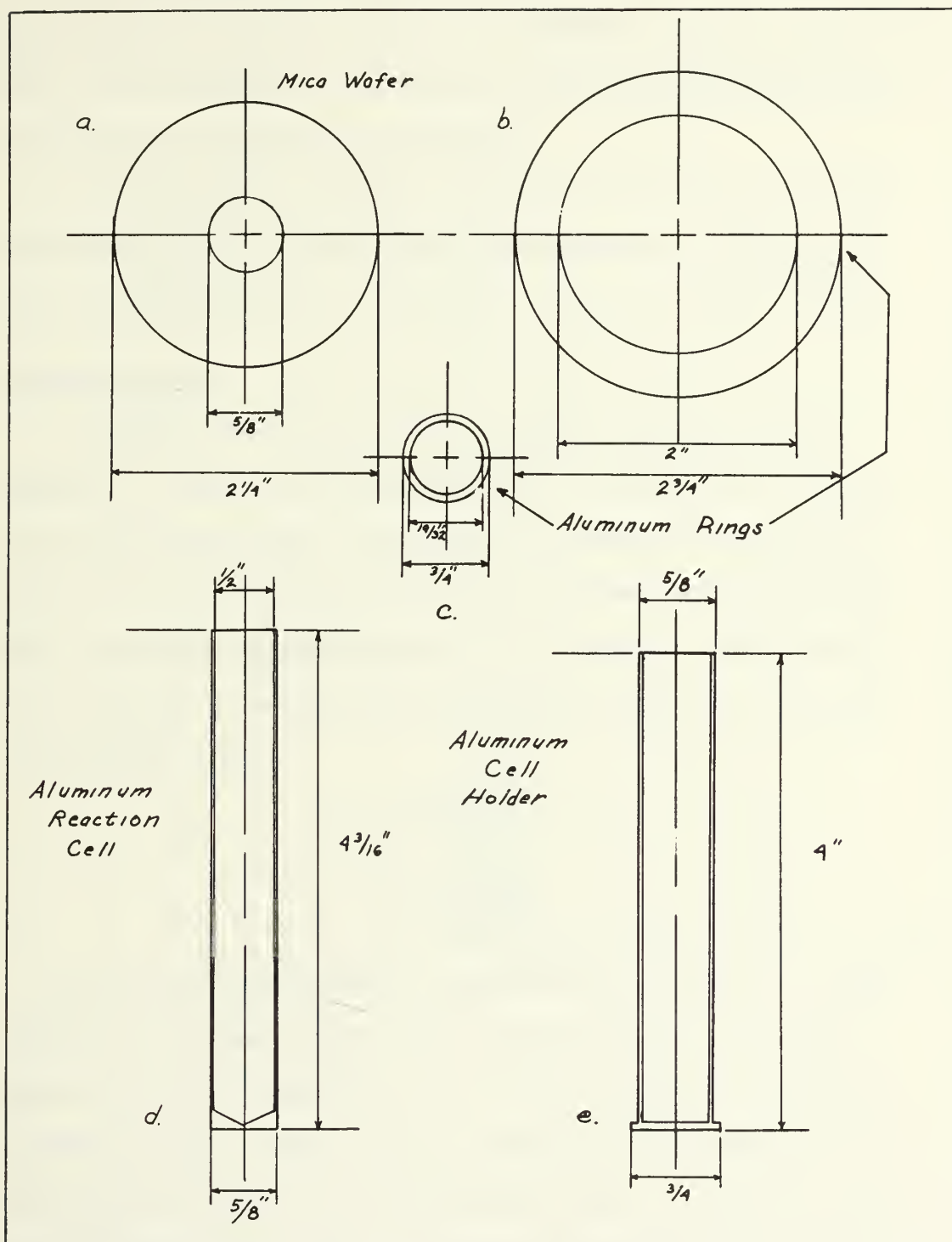


Fig. 7. (a) Mica wafer before wrapping with constantan wire, (b,c) Anodized aluminum rings, (d) Removable reaction cell, (e) Permanent cell holder, outside anodized.

Radiation Can and Shield

For protection against thermal fluctuation, a cast aluminum container and lid, 2 inches larger in all dimensions than the microcalorimeter, was constructed. The microcalorimeter sits inside this can on a small piece of marinite for insulation.

To protect against outside electrical interference the complete assembly was placed inside a large steel container, also with a lid. This electrically-grounded can reduces noise to a necessary minimum.

Calibration Coil

To determine the actual amount of energy released when the aggregate is immersed into the asphalt, it is necessary to calibrate the cell after each run. This is done by passing a known amount of electrical energy through a calibration coil immersed in the asphalt and recording the energy detected by the thermopile. The amount of energy released in microcalories per second is calculated by using the following formula:

$$\text{Rate} = \frac{I^2 R}{4.18}$$

I = miliamps

R = resistance of calibration coil in ohms.

The coil itself consists of approximately 36 inches of 30 gauge manganin wire wrapped around a small strip of mica, 1 3/4 inches long and 3/8 inches wide (Fig. 8). The total resistance of the coil is about 10 ohms. Copper wire was connected to the manganin wire for leads which are held in the teflon sample holder. Alligator clamps are used to connect these leads to extension wires coming out of the oven.

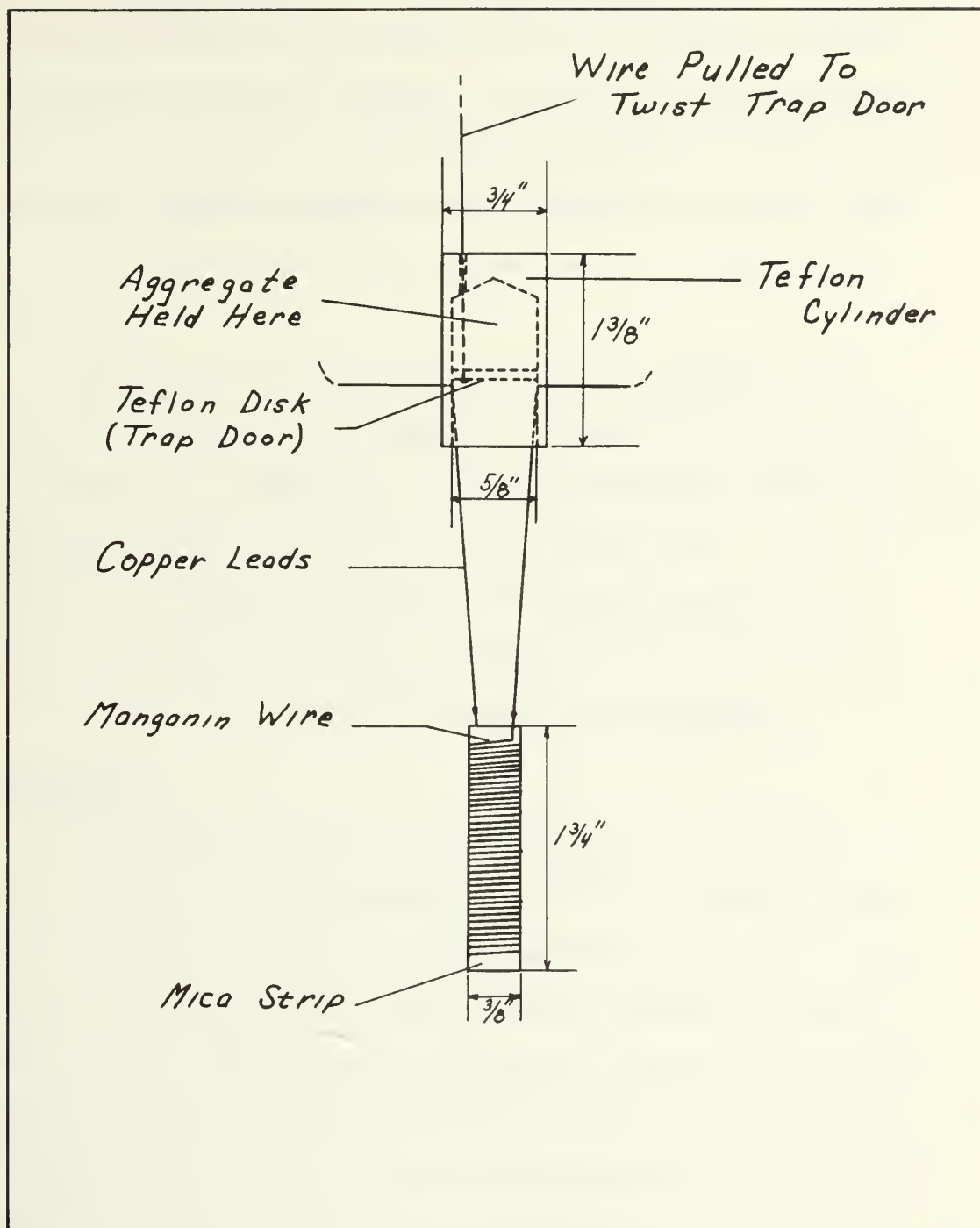


Fig. 8. Calibration coil. Small mica shelves (not shown) were attached to the coil to aid in dispersing the sample.

Teflon Sample Holder

The aggregate sample is held above the asphalt in a small circular teflon holder (Fig. 8). The holder fits over the reaction cell and is clamped on to prevent slippage. The aggregate is held in the container by a trap door--a teflon disk--and drops into the asphalt when the door is tripped by pulling a wire connected to the disk. There is a similar sample holder over the blank cell but no aggregate is held in it.

To be sure the trap door was tight enough to prevent asphalt vapors from getting into the aggregate container and adsorbing into the surface of the aggregate, an infrared spectrum was obtained on an aggregate which had been held over the asphalt under operating conditions. A comparison was made to an infrared spectrum of an aggregate which was not exposed to asphalt. This indicated that no, or very little asphalt had been adsorbed on the aggregate.

Electroplating

As previously discussed, the thermocouples were formed by electroplating copper on constantan wire.^(6,22) The electroplating was performed in a copper cyanide bath composed as follows: 4 ounces of basic copper carbonate, 5 ounces of sodium cyanide, 2 ounces of sodium sulfite, 1 ounce of sodium thiosulfite, and 1 gallon of water. The sodium cyanide and sodium sulfide were mixed with two-thirds of the water. A small portion of this solution was put in a clean container and the copper carbonate was added forming a thin paste. This paste was transferred back into the first solution and the remainder of the water was added. Then the sodium thiosulfate was added.

plus 2 ounces of sodium cyanide.

The electroplating was performed in continuously agitated baths at a temperature of 5° to 10° C, at a current density of 5 amperes per square foot, and at a voltage of 2 to 4 volts. After a thermopile was electroplated, it was dipped in dilute hydrochloric acid. The deposit produced was very hard and approximately 1/20 of a millimeter thick.

Anodization

Due to the fact that many components of the system are in direct contact with the thermopile, a type of insulation was necessary which would allow heat to flow readily but also be electrically non-conductive. Anodization proved to be the solution to the problem. This was accomplished in the procedure described below and is similar to a process discussed in Vol. 2 of the Metals Handbook (28).

The bath was a 15% sulfuric acid solution saturated with oxalic acid. The anodization took place at a temperature of 5° to 10° C and at a current density of 1 ampere per square inches for approximately 1/2 hour in continuously agitated baths. The baths were cooled by circulating ice water through copper coils placed in them. This process produced a very hard, thin insulating layer of aluminum oxide on the surface of the aluminum. The pieces of equipment that had to be anodized were the reaction cell holder, both large and small rings, and the inside surface of the sleeves.

PROCEDURE AND RESULTS

Experimental Procedure

The materials used at present in a standard experiment are asphalt No. B3036, a metal-amine additive, and the following aggregates all of the size -35 +48 M -- pure quartz, pure calcite, slag from a phosphate plant, two aggregates from Glacier County, one from Teton County and one from Lewis and Clark County. The last four were supplied by Mr. Weber of the Montana State Highway Department with the results of their stripping test for the four aggregates.

The present method of sample preparation is to crush the aggregate and obtain the -35M +48 M size fraction by screening with Tyler screens. This material is washed and dried at 160° C for approximately two hours. (In previous methods the aggregate was dried at 400° C for 12 hours under a vacuum of 10^{-6} mm pressure. No difference was detected). All samples are stored in plastic weighing vials over phosphorous pentoxide.

In a typical run a measured volume of asphalt weighing approximately 5 grams is placed in the reaction cell. A slightly smaller amount of the same asphalt is placed in the blank cell. The calibration coil is attached to the sample holder in which is contained a weighed amount of aggregate (0.4 gm to 0.5 gm). This assembly is placed in the reaction cell, and the calibration coil lowered into the asphalt, as the sample holder is attached to the cell. A small hose clamp keeps the sample holder firmly attached to the reaction cell.

The reaction cell assembly is placed in the cell in the micro-calorimeter situated in the oven preheated to 150° C. The system

is allowed 72 hours to reach equilibrium; after equilibrium is attained, the trap door is tripped and the aggregate falls into the asphalt.

The reaction is allowed to proceed for three hours or longer. The system is then calibrated (see Figs. 9 and 10 for calibration) and the cell is removed to be cleaned and inspected. The cell and calibration coil are cleaned with carbon disulfide in an ultra-sonic cleaner in preparation for the following run.

The metal-amine is an additive designed to increase the adhesion of the asphalt to the aggregate which was supplied to us by the State Highway Department. It was added to the test asphalt in concentrations of 1.0% amine by weight.

Discussion of Results

Curves for eleven different systems are seen in Figs. 11 to 21. The ordinate is the energy released in microcalories per second per gram of aggregate and the abscissa is time expressed in minutes. We were not successful in measuring the surface area of the aggregate. The B.E.T. method was attempted using nitrogen as the adsorbate. Should area data for -35 +48 aggregate become known, the curves could be easily converted to microcalories per gram per square meter, a more desirable unit. An approximate value of .03 sq m/gm was kindly supplied to us by Dr. W. H. Wade in the Chemistry Department at the University of Texas.

A blank was obtained to determine the relative amount of energy when the teflon door is tripped and aggregate falls into an empty cell. The energy released was negligible and would probably be fairly consistent for most runs.

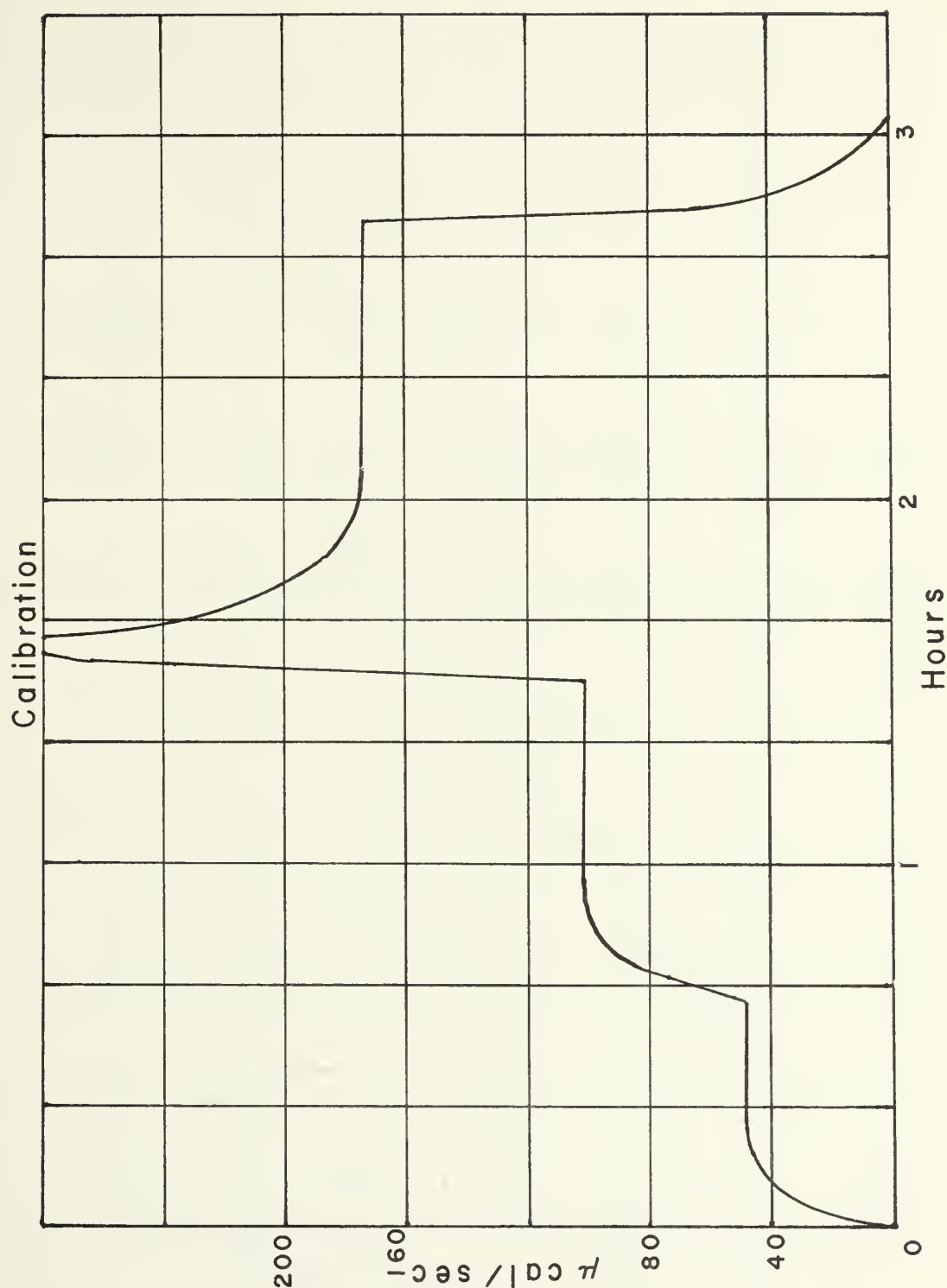


Fig. 9. The response to passing electrical energy through the calibration coil is seen. The curve is similar to that produced by the recorder during calibration. The plot is actually $I^2R/4.18$ vs time for the steady state or the plateaus.

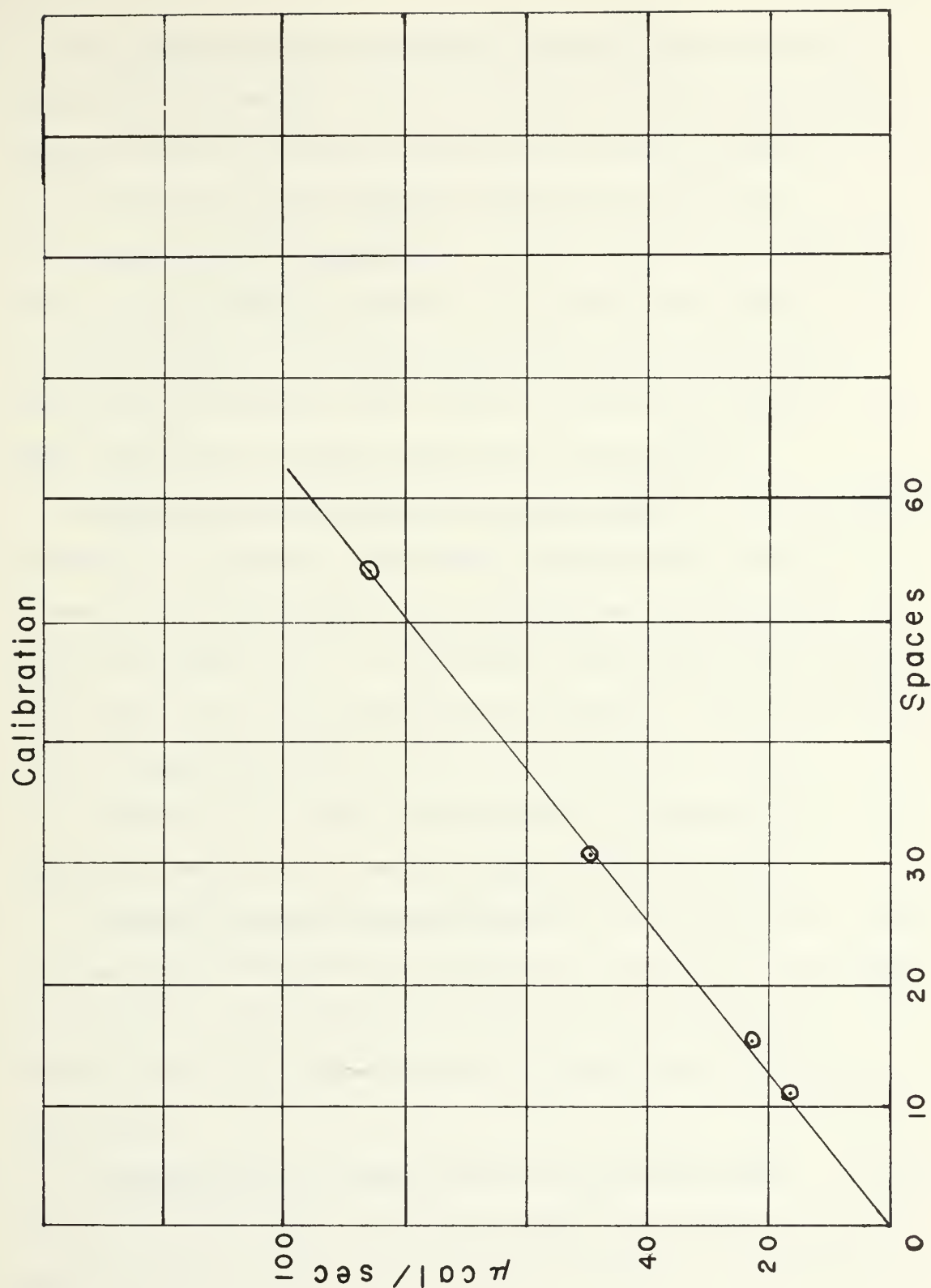


Fig. 10. The values for $I^2R/4.18$ at the plateaus are plotted against the spaces on the chart paper. (These are not necessarily the plateaus seen in Fig. 9.)

Most curves represent an average of three or four runs except pure quartz into asphalt. All of our initial work was in the quartz-asphalt system only and many runs were made using this system.

A discussion of the individual systems will now follow.

Quartz into Untreated Asphalt: In Fig. 11 is seen a typical curve for pure quartz immersed in asphalt. The initial peak height was consistently between 100 and 120 M cal/sec/gm although curves below and above this value were found. The tail was usually between 10 and 20 M cal/sec/cm, even after 15 hours for some reactions.

Quartz into Asphalt Treated with 1% Metal-amine: Fig. 12 represents the immersion of quartz in the asphalt which had been treated with a 1% metal-amine (Batch one). (No information has been obtained to the type of metal-amine used). The increase in the initial peak height was appreciable but the tail increase was much larger. In Fig. 12 the tail was about 40 M cal/sec/gm.

A second batch of amine treated asphalt was prepared and for unexplained reasons the tail was even higher as seen in Fig. 13.

Phosphate Slag into Untreated Asphalt: Fig. 14 represents a sample of slag from the phosphate plant near Butte. The curve is very similar to quartz with a tail slightly lower than a typical quartz curve. A road was constructed of this material near Butte and has given good performance.

Phosphate Slag into Asphalt Treated with 1% Metal-amine: The addition of the metal-amine increased the initial peak-height by about 30 M cal/sec/gm as seen in Fig. 15, but the increase in tail-height was roughly four-fold.

Glacier County No. 1 Aggregate into Untreated Asphalt: Glacier County No. 1 aggregate had given a strip test of only five percent adhesion. We found a very large initial peak, (Fig. 16), over 280 M cal/sec/gm, but a tail approaching that of quartz. This and other runs indicate the height of the tail correlates better with strip tests rather than the magnitude of the initial peak.

Lewis and Clark County Aggregate into Asphalt Treated with 1% Metal-amine: Strip tests using this system showed an improvement from untreated to treated of 5% to 98%. We detected a 2 to 3 fold increase in tail-height as seen in Fig. 18.

Glacier County No. 3 into Untreated Asphalt: Glacier County No. 3 had shown an 85% adhesion with untreated asphalt. Fig. 19 shows a tail-height of 30 M cal/sec/gm. Again there is a correlation between tail height and strip-test measurements.

Teton County Aggregate into Untreated Asphalt: In Fig. 20 is seen the highest tail on a curve for aggregates in untreated asphalt. It is interesting to note that other aggregates gave higher initial peaks but much lower tails. Strip-tests had shown a 95% adhesion.

Pure Calcite into Untreated Asphalt: Since calcite has been used as a filler we thought it might be of interest to investigate its immersion in asphalt. It gave an unusual curve (Fig. 21) in that the initial peak was similar to quartz but an unusually high tail with a slight upward slope was noted.

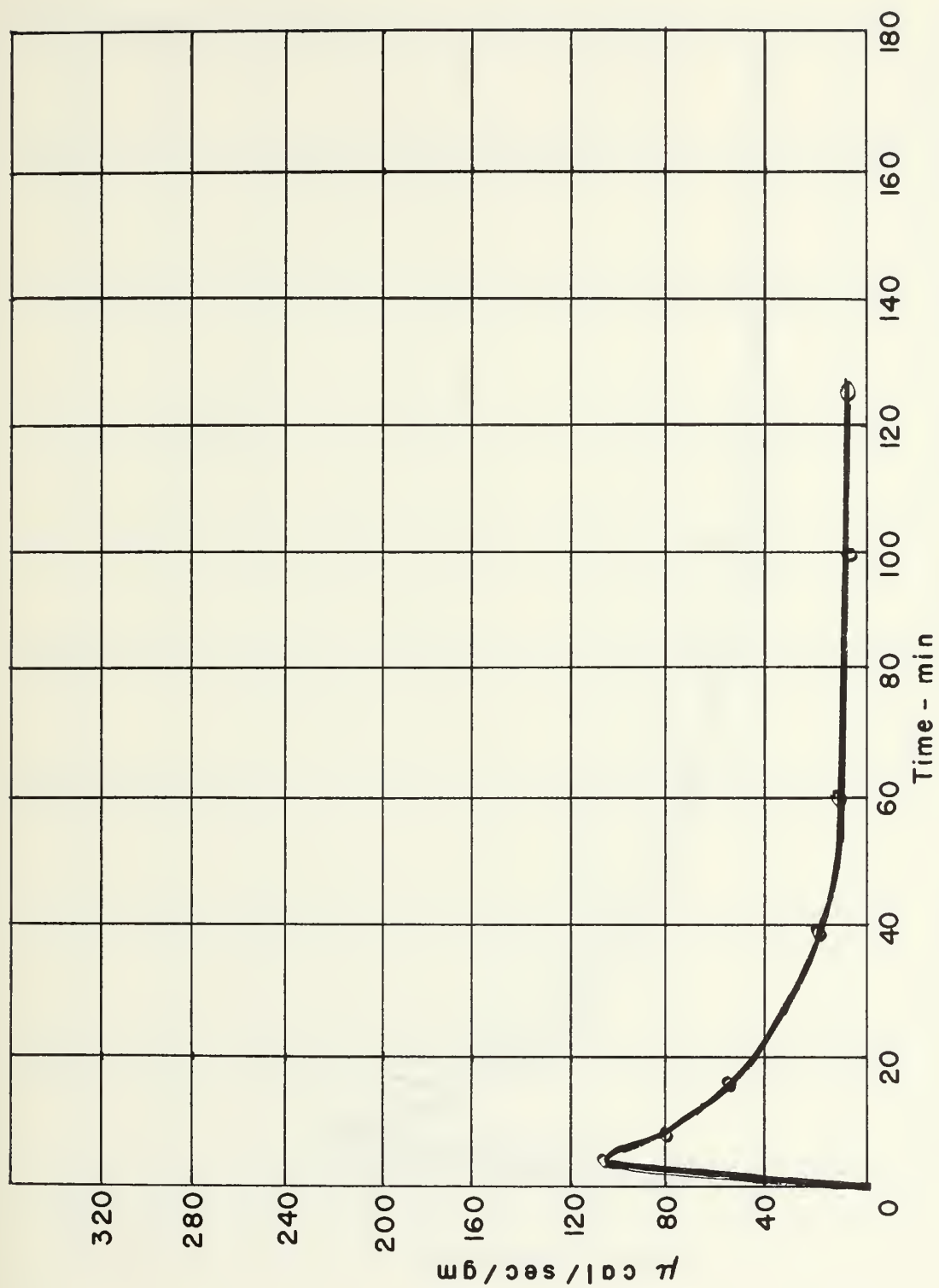


Fig. 11. Immersion of Pure Quartz in Untreated Asphalt, B-3036.

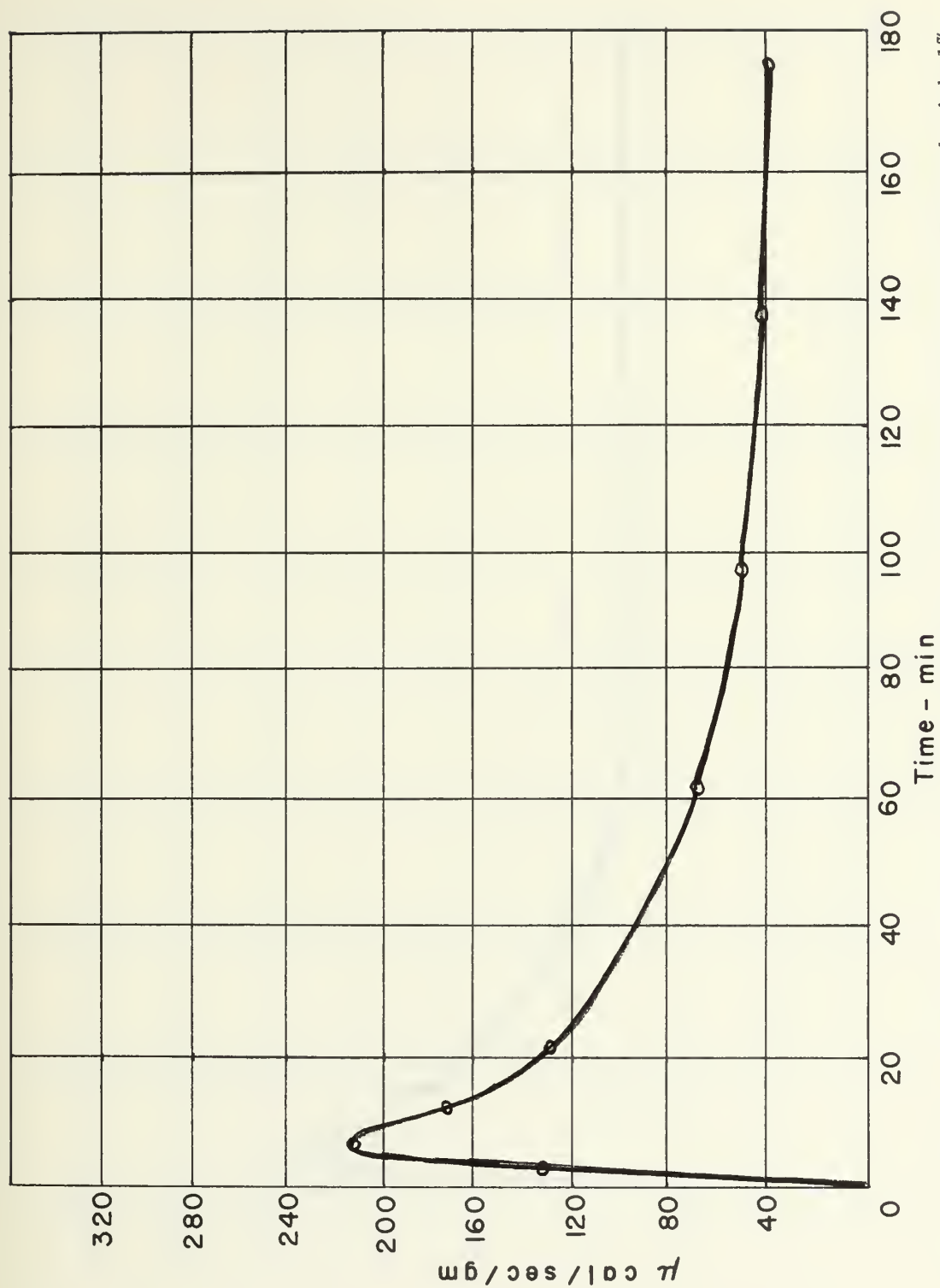


Fig. 12. Immersion of Pure Quartz in Asphalt, B-3036, Which Has Been Treated with 1% of the Metal-amine. Batch 1.

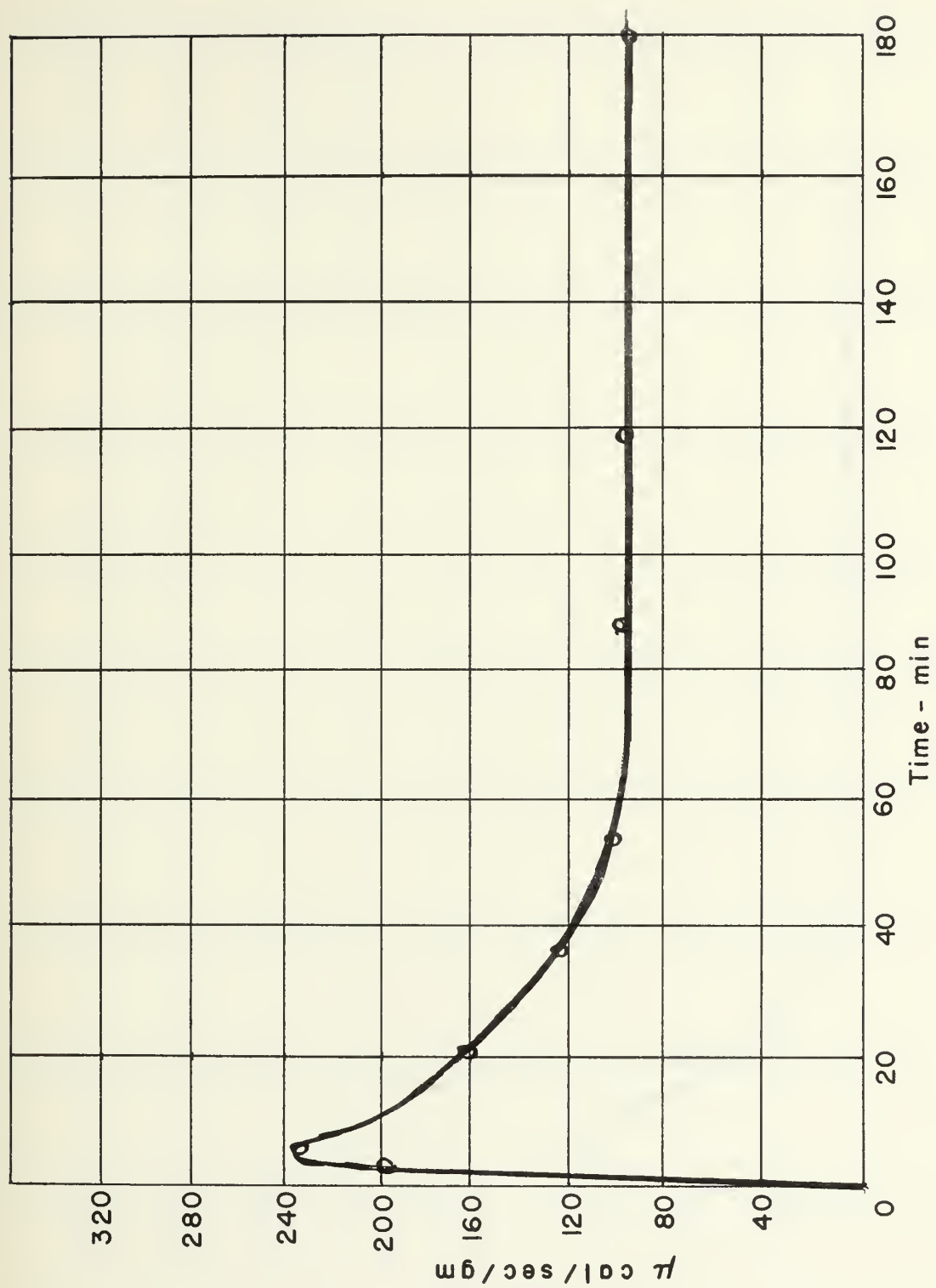


Fig. 13. Immersion of Pure Quartz in Asphalt, B-3036, Which Has Been Treated with 1% of the Metal-amine. Batch 2.

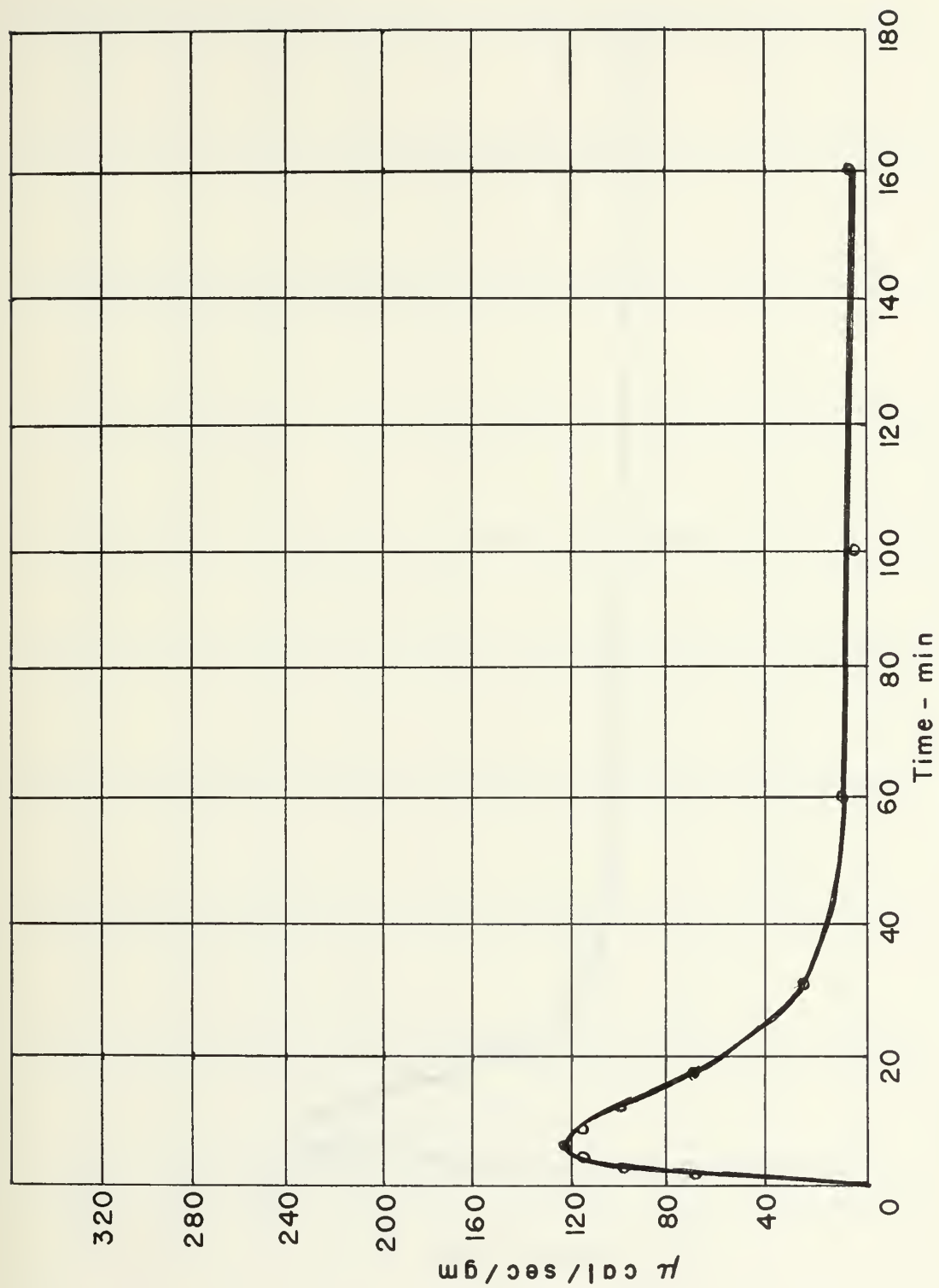


Fig. 14. Immersion of a Phosphate Slag in Untreated Asphalt, B-3036.

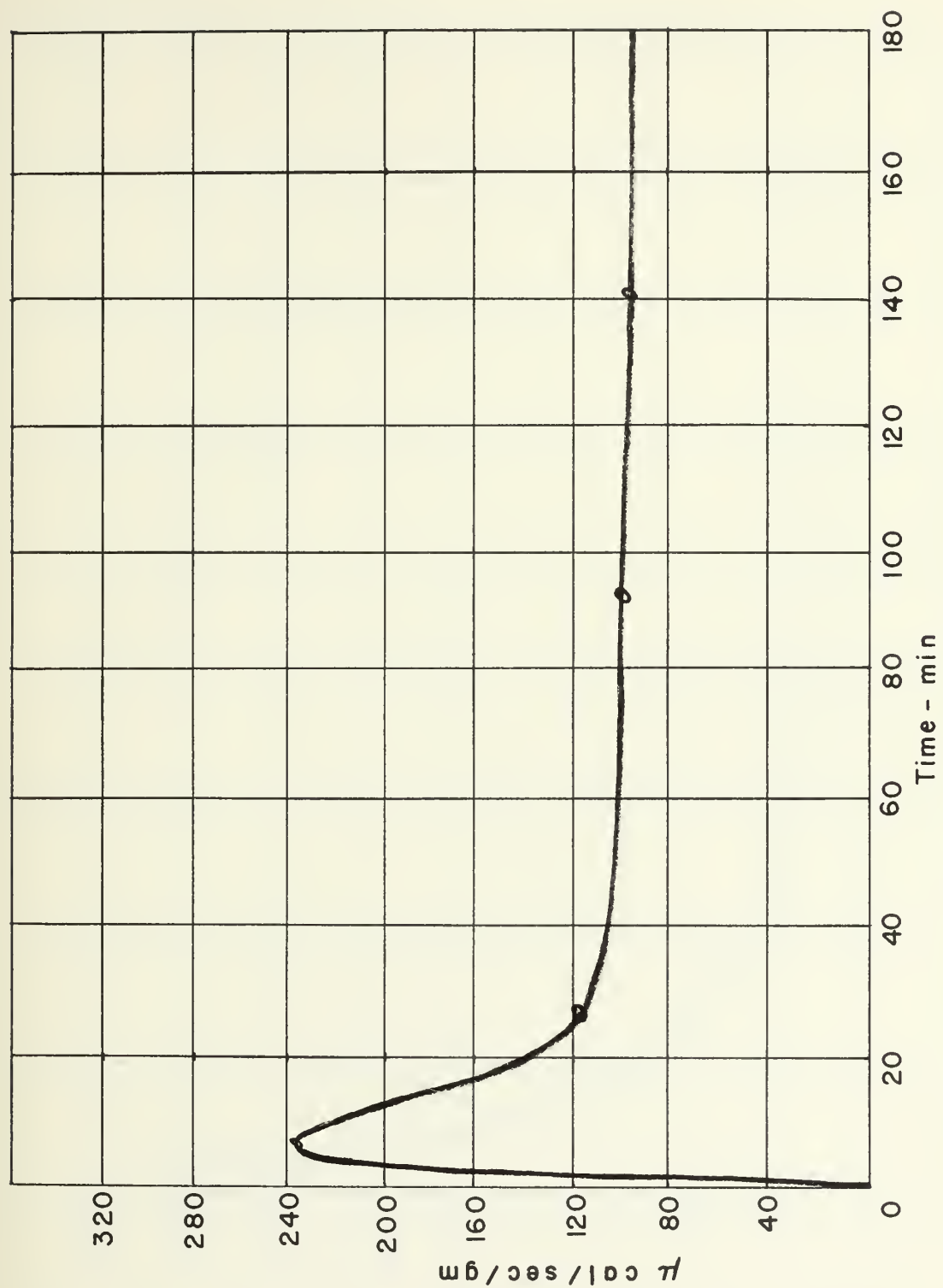


Fig. 15. Immersion of Phosphate Slag in 1% Metal-amine Treated Asphalt.

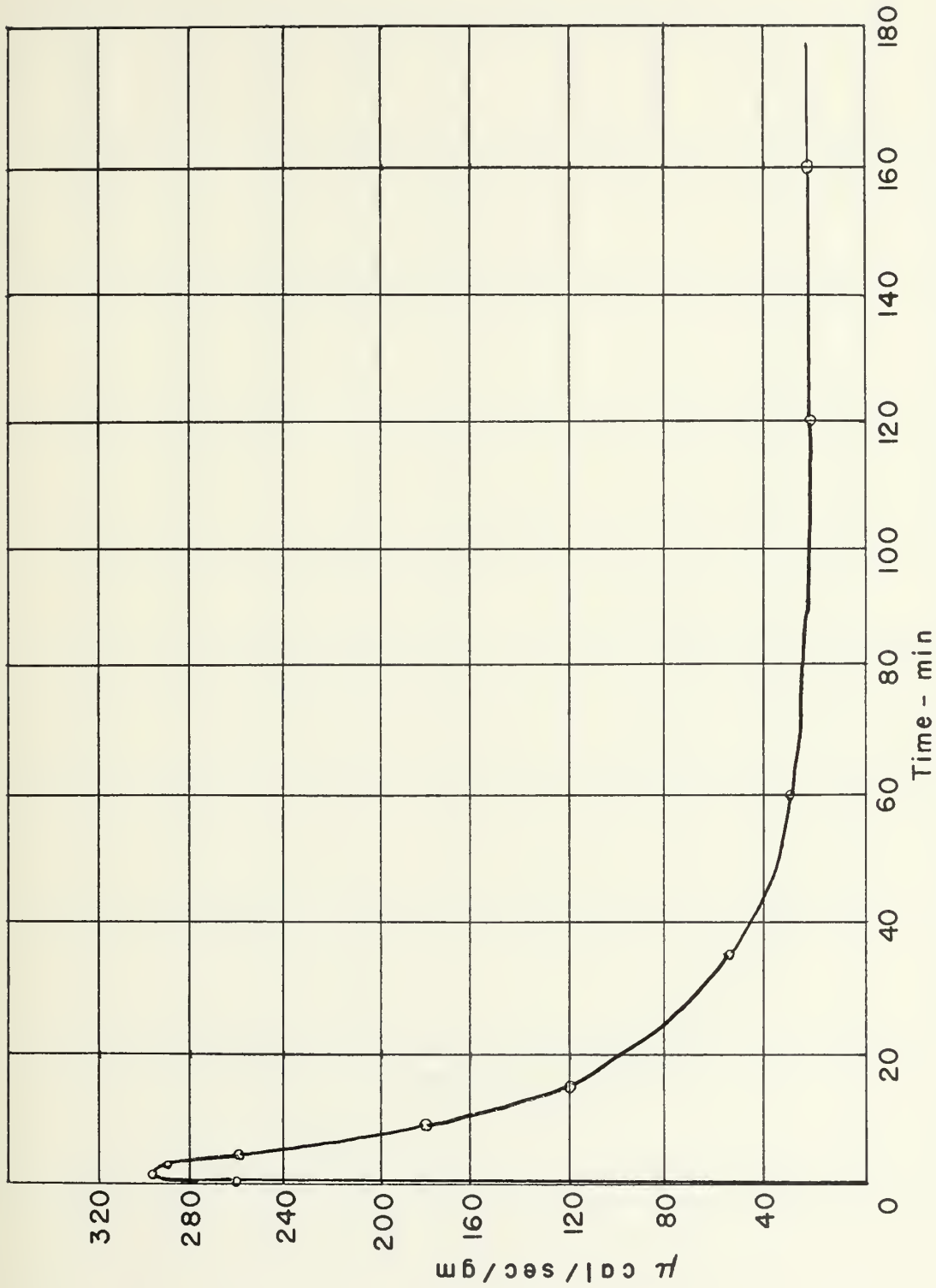


Fig. 16. Immersion of Glacier County No. 1 Aggregate in Untreated Asphalt B-3036.

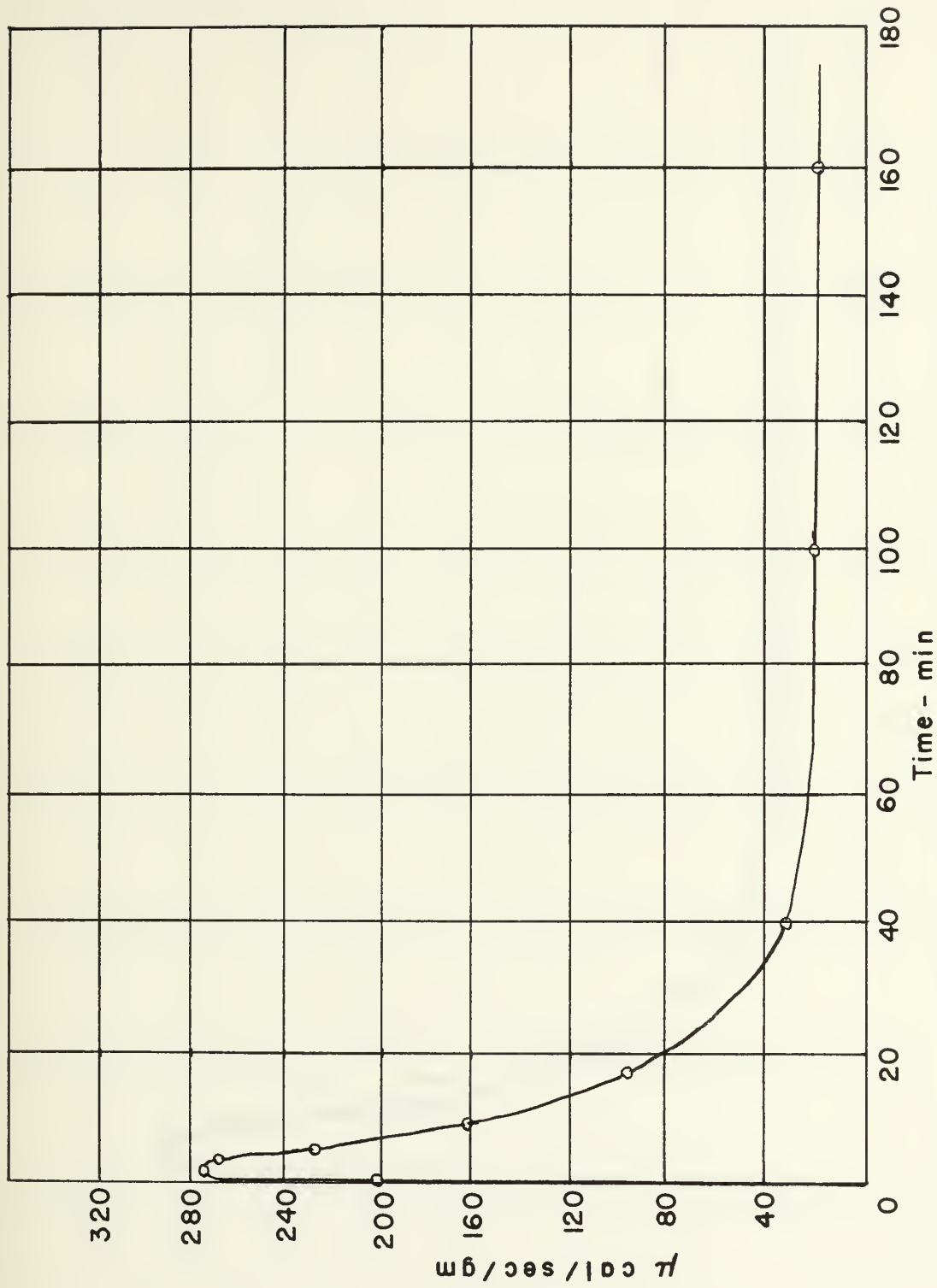


Fig. 17. Immersion of Lewis and Clark County Aggregate in Untreated Asphalt, B-3036.

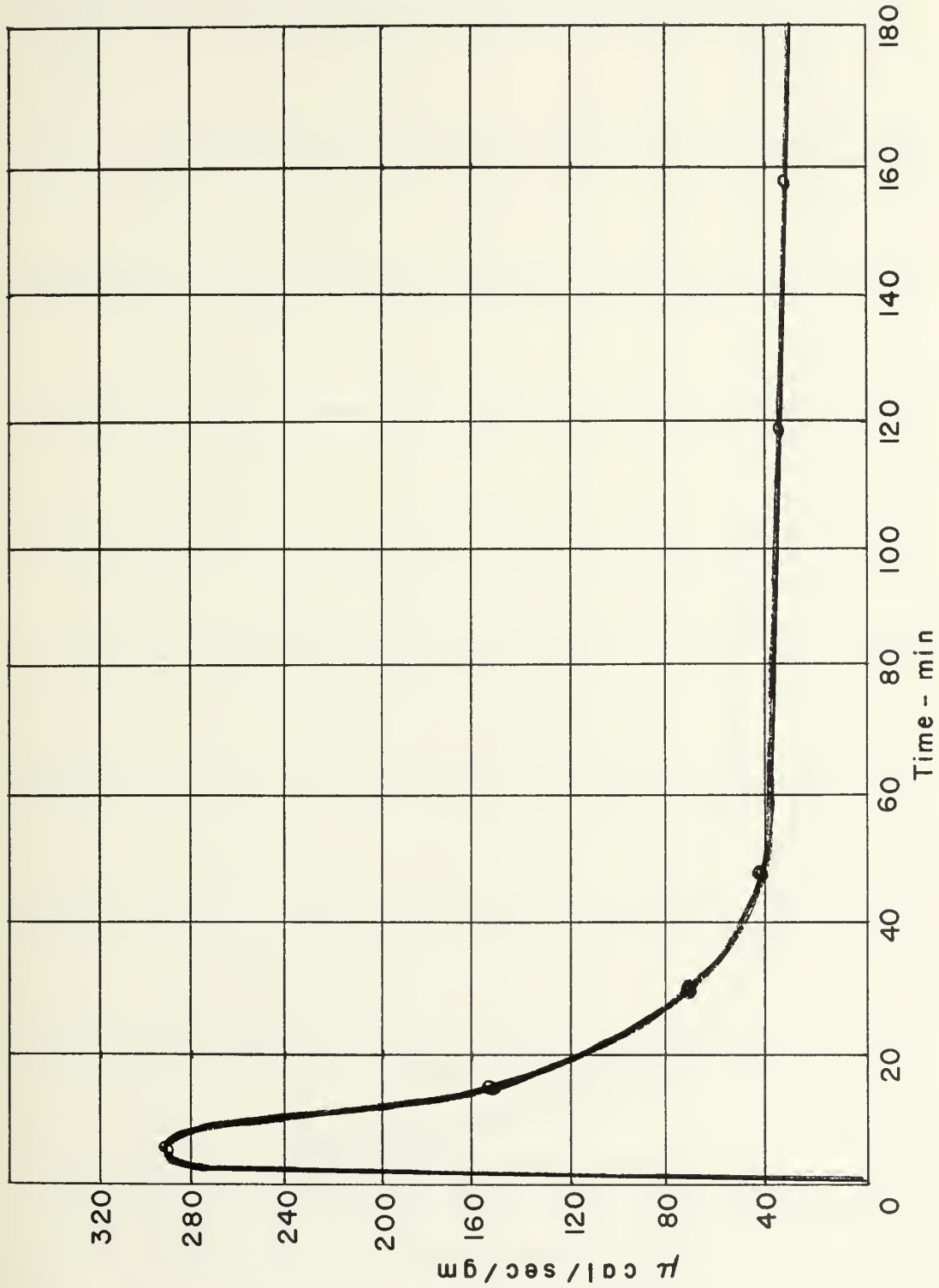


Fig. 18. Immersion of Lewis and Clark County Aggregate in 1% Metal-amine Treated Asphalt.

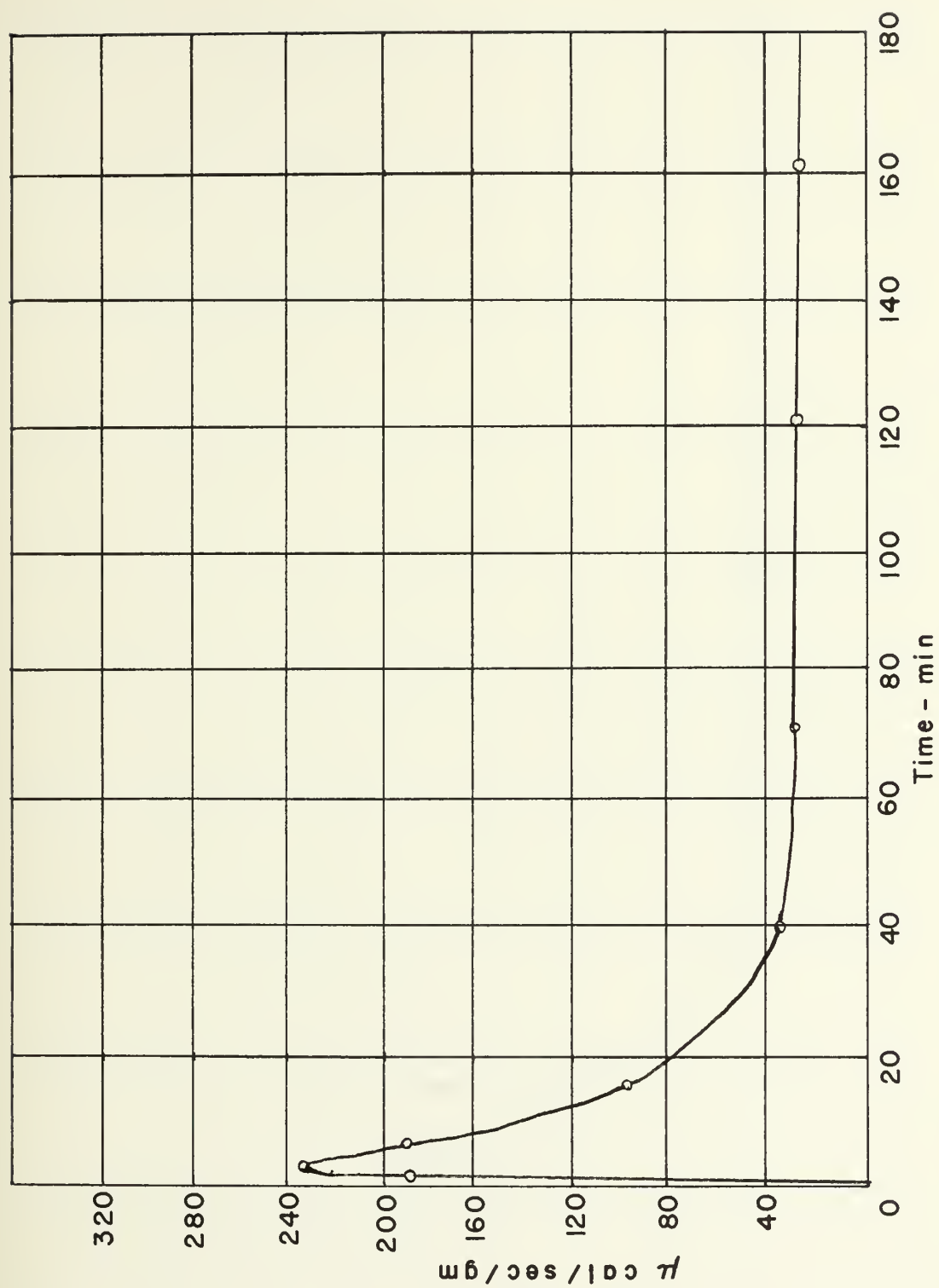


Fig. 19. Immersion of Glacier County No. 3 Aggregate in Untreated Asphalt, B-3036.

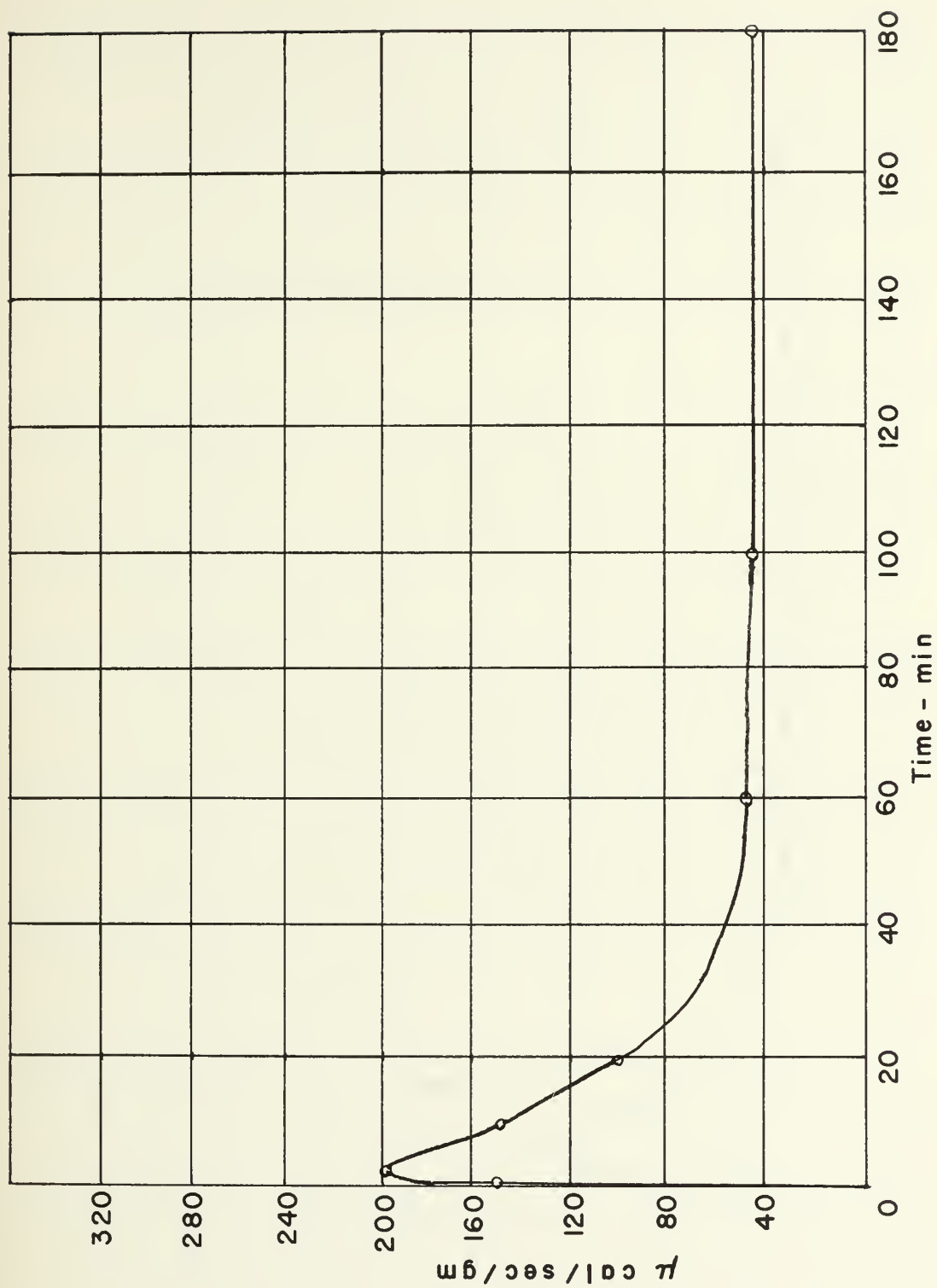


Fig. 20. Immersion of Teton County Aggregate in Asphalt B-3036.

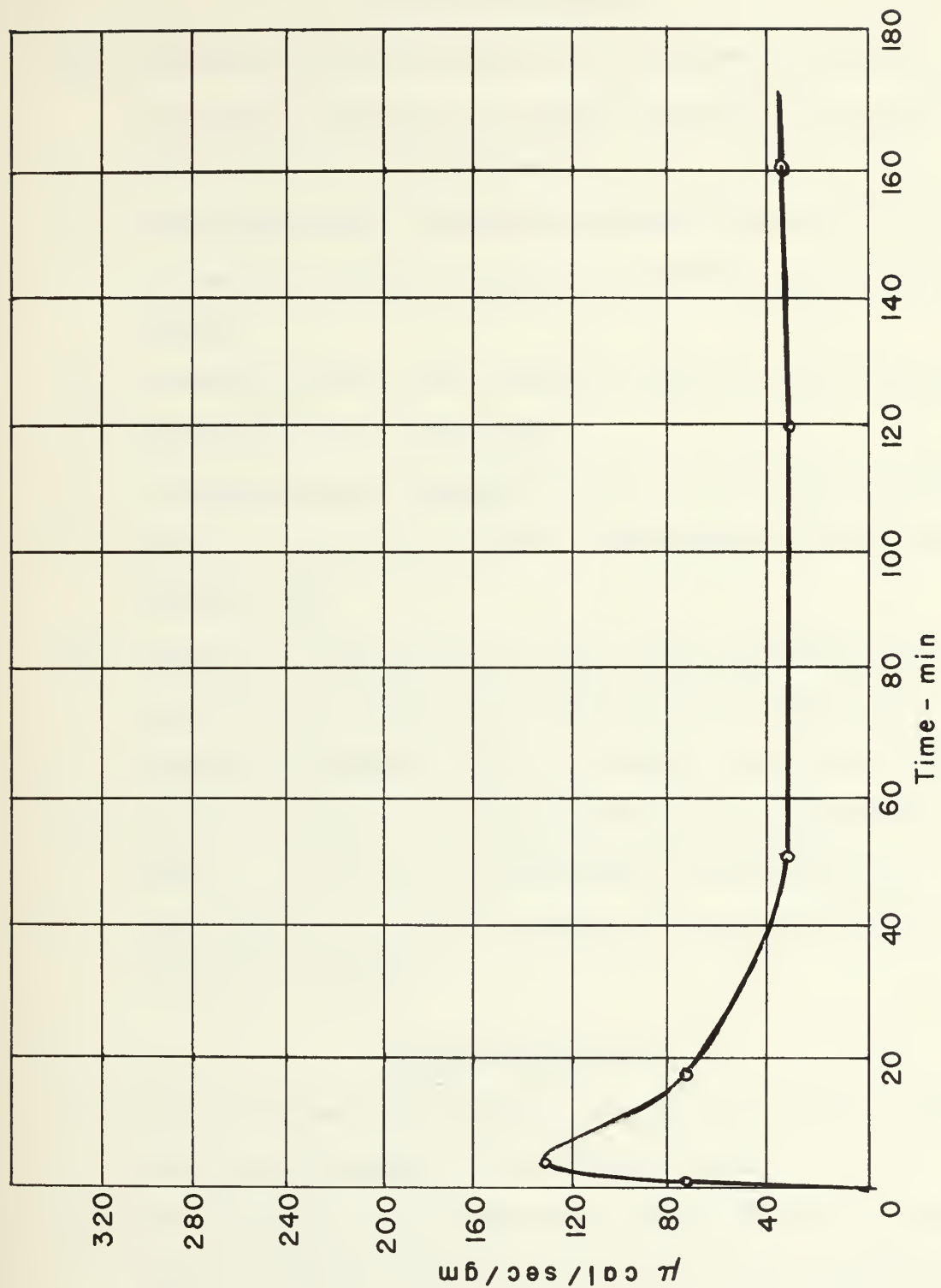


Fig. 21. Immersion of Pure Calcite in Untreated Asphalt B-3036.

GENERAL CONCLUSIONS

- (1) The constructed microcalorimeter is an extremely sensitive instrument and capable of measuring the energy released in the bonding process between asphalts and aggregates.
- (2) The microcalorimeter can easily distinguish between the energies released when different aggregates are immersed into the same asphalt.
- (3) The energy released in the immersion process is very dependent upon certain additives to the asphalt.
- (4) In comparing heat of immersion curves to the strip-test measurements the tail-height is directly proportional to the asphalt-aggregate bond.
- (5) Adsorption of asphalt on the various tested aggregates is a slow phenomena and probably would continue for many hours if the asphalt and aggregate are held in contact at high temperatures.
- (6) As a final conclusion we are proposing that the initial peak height is a function of the properties of adhesion and the tail height is a function of cohesion between the multilayers surrounding the aggregate.

SPECIFIC CONCLUSIONS

- (1) Calcite, Teton County aggregate, and Glacier County No. 3 aggregate gave the best bonding with test asphalt, B3036.
- (2) The 1% addition of the metal amine greatly improved the bonding with quartz, phosphate slag and Lewis and Clark County aggregates.

RECOMMENDATIONS FOR HIGHWAY CONSTRUCTION

- (1) Maintain high mixing temperatures as long as economically possible to allow maximum asphalt build-up on the aggregate.
- (2) With the aid of the microcalorimeter test several aggregates in a given geographical location for optimum bonding with the asphalt being used.
- (3) Test several additives for each asphalt-aggregate system using the microcalorimeter.
- (4) Use finely divided material for filler to obtain a large surface area which takes maximum advantage of the adsorption process.

RECOMMENDATIONS FOR FUTURE HEATS OF IMMERSION STUDIES

- (1) The surface area for each aggregate should be determined.
- (2) Immersion studies at other temperatures should be investigated.
- (3) Other asphalts, aggregates, additives and fillers should be investigated.
- (4) The effect of water in the asphalt should be studied.
- (5) Pretreatment of aggregates with various metal ions should be investigated.

LIST OF REFERENCES

1. Le Maire, G. W. "A Study of Asphalts and Asphaltic Materials" Quarterly of the Colorado School of Mines, Vol. 48, No. 2, 1953.
2. Barth, E. J. Asphalt Science and Technology, Gordon and Breach Sci. Pub., New York, N. Y., 1962.
3. Abraham, H., Asphalts and Allied Substances, Vol. 1, 6th ed., van Nostrand, New York, N. Y., 1960.
4. Wronka, J. A. "Asphalts" Anal. Chem. Annual Reviews, Vol. 39, No. 5, p. 165R, (1967). [Ibid, Vol. 37, No. 5, p. 150R (1965)].
5. Zettlemoyer, A. C. "Immersional Wetting of Solid Surfaces" Chemistry and Physics of Interfaces, Symposium sponsored by Industrial and Engineering Chemistry, S. Ross, Chairman, 1964.
6. Calvet, E. and Prat, H., Recent Progress in Microcalorimetry, Trans. and ed. by H. A. Skinner, MacMillan Co., New York, N. Y., 1963.
7. Zettlemoyer, A. C., and Young, G. J. and Chessick, J. J. "A Thermistor Calorimeter for Heats of Wetting: Entropies from Heats of Wetting and Adsorption Data" J. Phys. Chem. 57, 649 (1953).
8. Bernett, M. K., and Zisman, W. A., "Surface Chemical Displacement of Organic Liquids from Solid Surfaces" J. Phys. Chem., 70, 1064 (1966).
9. Moelwyn-Hughes, E. A., Physical Chemistry, Sec. Rev. Ed., Pergamon Press, New York, N. Y., 1961, p. 180.
10. Adamson, A. W., Physical Chemistry of Surfaces, Interscience Pub., New York, N. Y., 1960.
11. Copeland, L. E. and Young, T. F., "A Thermodynamic Theory of Adsorption," Solid Surfaces and the Gas Solid Interface. Advances in Chemistry Series 33, R. F. Gould, Ed., (1961) p. 348.
12. Fowkes, F. M., "Dispersion Force Contribution to Surface and Interfacial Tension, Contact Angles and Heats of Immersion", Contact Angle, Wettability and Adhesion, Adv. in Chemical Series 43, R. F. Gould Ed., (1964) p. 99.
13. Danielli, J. F., Pankhurst, K. G. A. and Riddiford, A. C., eds., Surface Phenomena in Chemistry and Biology, Pergamon Press, 1958.
14. Alner, D. J., Aspects of Adhesion, Univ. of London Press Ltd., London, 1965.

15. Harkins, W. D., Physical Chemistry of Surface Films, Reinhold, New York, N. Y., 1952.
16. Lindstrom, L., "Bonding of Amines to Silicates" Scandinavian Symposium on Surface Activity 2nd, Ekwall, P, Groth, K., Runnstrom-Reid, V, Eds., Academic Press, New York, N. Y., 1965.
17. Snyder, L. R. and Ward J. W. "The Surface Structure of Porous Silicas" J. Phys. Chem. 70, 3971 (1966).
18. Silberberg, A., "Adsorption of Flexible Macromolecules. III Generalized Treatment of the Isolated Macromolecules; The Effect of Self-Exclusion" J. of Chem. Phys., 26, 1105 (1967).
19. Shulman, J. H. "Oppositely Charges Mixed Collectors in Flotation" (16:7).
20. Brown, B. W., and Welby, C. W., "Improvement of Sands and Gravels for Use with Asphalts" Conducted by the University of Southern Mississippi (1965).
21. Wade, W. H., and Hackerman N. "Thermodynamics of Wetting of Solid Oxides", (12:22)
22. Wilson, W. H., and Epps, T. D. "Construction of Thermocouples by Electrodeposition," Phys. Soc. (London) Proc., 32, 326 (1920).
23. Benzinger, T. H. and Kitzinger, C., Temperature: Its Measurement and Control in Science and Industry, Hertzfeld, C. M. ed., Reinhold Pub. Corp., New York, N. Y., 1963.
24. Sharpe, L. H., Schonarn, H., and Lynch, C. J. "International Science and Technology" April, 1964, p. 26.
25. Hemberg, B., "Adhesion - A Fundamental Force" (16:285)
26. Debye, P. J. W. "Interatomic and Intermolecular Forces in Adhesion and Cohesion", Adhesion and Cohesion, P. Weiss ed., Elsevier Publishing Co., New York, N. Y., 1962, p. J.
27. Rowland, F., Bulas, R., Rothstein, E. and Eirich, F. R., "Structures of Macromolecules at Liquid-Solid Interfaces" (5:109).
28. American Society of Metals. Metals Handbook. Vol. 2, 6th ed.

